MICRO-GALVANIC CORROSION CELLS
ASSOCIATED WITH SiC / Al MMCs

A Thesis Presented to The University of Surrey
for The Degree of Doctor of Philosophy

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October 1995
ABSTRACT

The corrosion of SiCp/6061 Al in 3% NaCl solution, at pH values of 3.8, 7.2 and 10.2, has been studied using SEM and combined scanning Auger electron/X-ray microscopy. The MMC, fabricated by powder metallurgy, contains approximately 15 percent (volume) SiC as ≤10 μm particles. Scatter diagrams are applied to analyze elemental maps created by scanning Auger microscopy. The experiments reveal that some impurity elements such as Fe, Ti etc., introduced during fabrication, form intermetallic compounds and that these are the dominant factors causing micro-galvanic corrosion. The Auger maps show, by inspection, that oxygen is enriched after exposure around these intermetallics. This has been confirmed by using scatter diagrams to analyze the data contained within the map. The phenomenon is probably caused by the dissolution of aluminium, resulting in the deposition of porous corrosion products such as Al(OH)₃ and AlOOH.

Because of a low overpotential for oxygen reduction, the intermetallic compounds are expected to act as cathodes. This is confirmed by the finding of magnesium hydroxide on the surface of the intermetallics after exposure of the specimen in MgCl₂ solution. It is shown that the onset of this deposition can be used to estimate the cathodic current density at the cathode. Current density at the SiC particles, estimated by this method is negligible, suggesting that the principal cause of corrosion is found in the interaction between the aluminium alloy and the intermetallics.

The same method is used for SiC₃/6061 Al MMC. Intermetallic particles are found much more likely to be located at a fibre/matrix interface, and they are still a sensitive factor for localized corrosion. There is some Cr in the Fe-containing intermetallics in this matrix, this type of intermetallic is not very susceptible to micro-galvanic corrosion. Another different aspect is that the reinforcing material in SiC₃/6061 Al MMC is directly associated with the micro-corrosion cell. The
reinforcing SiC fibre belongs to the SCS series which consists of three different layers. The SiC is grown on a carbon core by chemical vapour deposition and a protective coating is applied on the outside of the fibre. This coating is mainly composed of carbon which is slightly enriched in silicon at the surface. In this investigation we found that carbon core and carbon coating act as cathodes and form a galvanic cell with surrounding aluminium alloy. This is confirmed by the magnesium decoration method.

Electrochemical techniques are also used. Several kinds of SiC fibres and graphite fibres are cathodically polarized in 3% NaCl solution. By comparison with the anodic polarization curve of Al alloy, the galvanic cells between Al alloy and carbon core or protective coating are confirmed. There is no galvanic effect between Al and pure SiC. Al$_3$Fe is extracted from intermetallic enriched Al alloy, and the electrochemical performance of this intermetallic is investigated.
ACKNOWLEDGEMENTS

I would like to express my greatest thanks to my supervisor, Professor J. E. Castle, for his constant encouragement, advice and patience throughout this work.

I am also indebted to Dr J. F. Watts and my other colleague in the Surface & Interface Research Group, namely, M. Baker, A. Brown, S. Greaves, P. Zhdan, S. Davis, S. Jenkins, X. Yang, and A. Taylor. The numerous helpful discussions combined with their advice and support have been invaluable during the course of this work. The assistance of technical staff in the department of Materials Science & Engineering has been a great help. Acknowledge to Dr Steven Harris of BAE for the helpful discussion and provision of small samples of the materials used in this work. Thanks to Dr P. Tsakiropoulos and other colleague in his group for providing special specimens for this work.

I am grateful to the Committee of Vice-Chancellors and Principals of the Universities of the United Kingdom for provision of Overseas Research Students Award and to SIR group for providing additional financial support.

Finally, I would like to offer my sincere thanks and appreciation for the support I have received from my family and in particular my husband, YAN Huan.
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Chapter 1 Introduction

Composite materials are combinations of materials put together to achieve a particular function. The idea of composite materials is not that recent. Nature is full of examples wherein the idea of composite materials is used. Bone is an example of a natural composite, which consists of short and soft collagen fibres embedded in a mineral matrix called apatite (Chawla, 1987). Besides the naturally occurring composites, there are many other engineering materials that have been in use for a long time. Straw reinforced mud bricks and various composite bows have been found in Egypt and Mongolia which have been dated to 2000 BC or earlier. However, composites as understood today really started with the development of the process of making strong glass fibres in the late 1930's and the development of the first commercial unsaturated polyester resins a little later (Bader, 1993).

Advanced metal matrix composites appeared from the development of boron and carbon fibres in the 1950-1965 period. The boron fibre reinforced 6061 aluminium matrix composite was developed in the 1960s. Carbon fibre reinforced metallic composites were successfully made in the 1970s. With the availability of a wide variety of SiC and Al$_2$O$_3$ reinforcements, the research activity in the area of metal matrix composites increased tremendously the world over.

Among all the metal matrix composites, aluminium matrix composite is the most common one due to its low density and excellent strength, toughness, and resistance to corrosion. The aerospace industry has been the major target of this development. It is particularly difficult to achieve good compatibility with an Al matrix, because Al readily interacts to form intermetallics with most ceramics, and it is also very difficult to achieve good wetting. SiC is essentially stable below the melting point of Al, although it reacts with most alloys at temperatures above the liquidus. Silicon carbide in a particulate or fibrous form has been incorporated in aluminium alloys.
In recent times metal matrix composites have attracted considerable academic and industrial attention. A large amount of research is orientated towards characterising mechanical properties and defining the relationship between those properties, microstructure and processing route. There are relatively few people concentrating on the corrosion behaviour. In general, the addition of a second phase to a metal alloy will change significantly the corrosion behaviour, such that any galvanic coupling within the materials will result in localized corrosion of the matrix. Aluminium based MMCs are generally considered to be more susceptible to corrosion attack than the matrix alloy in an unreinforced condition.

Many previous researchers have noted that the pitting potentials of SiC reinforced MMCs and the corresponding plain alloy are very similar. However, the presence of the SiC phase affects the growth of corrosion pits. The pits in MMCs are greater in number, smaller in size, and more shallow in penetration depth. Some researchers have attributed this difference to the greater number of intermetallic phases found in the composite when compared with the plain alloy. The smaller size of pits established on the composite surfaces suggests that the SiC reinforcement might interfere with or decrease the metal dissolution rate. Since the previous research is normally based on the electrochemical method, it is difficult to obtain, directly, information about micro-corrosion cells.

In this investigation, we set out to give positive identification of the operating cathodes in a typical MMC and, additionally, to estimate the current density associated with this electrochemical activity. The anodic and cathodic regions of the micro-corrosion cell are mapped out by using SAM, the cathodes being identified by use of magnesium ion decoration which occurs by precipitation of magnesium hydroxide. Identification of the chemical phases present on the surface is undertaken using Scatter Diagrams. In undertaking this work we called on the experience gained in the examination of micro-corrosion cells associated with inclusions in stainless steel (Castle and Ke 1990, Baker and Castle 1992). This work has shown that a high spatial resolution scanning Auger microscope combined with simultaneous EDX analysis is ideal for detection of the surface chemical
changes due to corrosion on the micrometre scale (Castle 1986, 1992). This technique has been used, successfully, to study pitting corrosion caused by inclusions in stainless steel.
Chapter 2  Literature Survey

2.1 METAL MATRIX COMPOSITE MATERIALS

As structural materials (Figure 2.1), metal matrix composites (MMCs) were initially of interest as a means of obtaining high strength, modulus and thermal stability, which were of particular interest to the aerospace industry, automotive, electronics and sporting goods. In general, composite materials have particular appeal because, within limits, they can be designed and fabricated to fit the mechanical requirements of a given application (Lloyd 1988 and Begg 1991).

![Figure 2.1](image)

Figure 2.1  One means of classification materials.

2.1.1 Classes of MMCs

A composite material can be defined as a material consisting of two or more
physically and/or chemically distinct, suitably arranged or distributed phases (Chawla, 1987). When the matrix component is a metal, we call such a composite a metal matrix composite (MMC). It is clear that the characteristics of MMCs are mainly dependant upon two principal components: the type of reinforcement used and the matrix materials. The early studies on MMCs were addressed to the development and behaviour of continuous fibre reinforced, high performance, hybrid materials which were based on aluminium matrices. More recently, the family of discontinuously reinforced MMC including both particulates and short whiskers or fibres has attracted considerable attention.

![Figure 2.2 Types of metal matrix composites (Carter and Paul 1991).](image)

**Reinforcement**

The reinforcement can be categorized into two groups, in terms of their shapes, which are those for continuous reinforcement and discontinuous reinforcement respectively. The discontinuous reinforcement can also be divided into (1) discontinuous short fibres, (2) whiskers and (3) particulates. Continuous
reinforcements give maximum strength, but unfortunately, they are very expensive, very directional, and can not be made by the usual metal working fabrication processes, such as extrusion, rolling and forging. Whiskers, because of their small diameters, have very few defects to initiate fracture and have much higher strengths than discontinuous fibres. The properties of discontinuous fibre are greatly inferior to those of continuous fibres, but the cost is much less. The cheapest form of reinforcement is particulate which makes MMCs more amenable to conventional metal processing methods and still gives useful enhancement of properties.

From the point view of materials for the reinforcement, silicon carbide, alumina, graphite and boron have been used for continuous fibre, $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ are employed for discontinuous fibre. The main commercially available whiskers are $\text{SiC}$ or $\text{Si}_3\text{N}_4$. Many different ceramics are readily available for the particulate reinforcement in a wide range of sizes, but those of interest for aluminium MMCs are $\text{SiC}$ and $\text{Al}_2\text{O}_3$.

<table>
<thead>
<tr>
<th>Table 2.1 The density of typical matrix materials and reinforcements</th>
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<td><strong>matrix materials</strong></td>
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<tr>
<td>----------------------</td>
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<tr>
<td>Al</td>
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<td>Mg</td>
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Matrix alloys
Low density matrix alloys, such as Mg, Al and Ti are widely used because most of reinforcements have densities above 3 g/cm$^3$ (Table 2.1). Thus, there will be a severe weight penalty if reinforcements are incorporated into the higher density
metals. To date most of the composite work has involved Al. The composition of reinforcements and matrix alloys are thought to be the principle key to the corrosion problems of MMCs.

2.1.2 Fabrication

Besides the selection and design of composite materials, their fabrication is one of the key steps in making MMCs available for use. It is different from conventional metal fabrication, since damage to the reinforcement, and in some cases, interfacial reaction, should be avoided. In addition, continuously reinforced composites have no secondary forming capability, and the fabricated shape must be the shape in which they are used.

Discontinuous reinforcement

Many kinds of materials can be used as discontinuous reinforcement as mentioned above, but in this project SiC particulate reinforced Al MMC is the main material that is investigated. SiC in particulate form has been available quite cheaply and abundantly for abrasive, refractory, and chemical uses. In this conventional process, silica in the form of sand and carbon in the form of coke are made to react at 2400°C in an electric furnace. The SiC produced in the form of large granules is subsequently comminuted to the desired size (Chawla, 1987).

Fabrication routes for discontinuously reinforced composites should avoid damage of the reinforcement and reaction with the matrix. Four methods have been used to make discontinuously reinforced MMCs: 1) powder metallurgy, 2) liquid metal infiltration of preforms-squeeze casting, 3) molten metal mixing, and 4) spray deposition.

Powder metallurgy fabrication method (PM) has been used extensively for SiC whisker and SiC particulate reinforced MMCs, and the Alcoa process is shown in Figure 2.3. These include sieving of the rapidly solidified powders, blending with
the reinforcement phase(s), pressing to approximately 75% density, degassing and final consolidation by extrusion, forging, rolling, or some other hot working method. Ibrahim et al (1991) gave results showing that powder metallurgy processed Al-SiC MMCs processed higher overall strength levels relative to the equivalent material processed by a liquid phase process; the elongation values, however, are lower.

Liquid metal infiltration has been used for SiC whisker and most extensively for discontinuous short fibres. In this process a molten alloy is introduced into porous ceramic preform, utilizing either inert gas or a mechanical device as a pressurizing medium. Solidification conditions need to be controlled to prevent solidification fronts meeting within the preform to give porosity.

Molten metal mixing methods are, in principle, the most direct and cheapest method of producing MMCs. In this process, a strong bond between the matrix and the reinforcement can be achieved by utilizing high processing temperatures and alloying the matrix with an element which can interact with the reinforcement
to produce a new phase and have a ‘wetting’ effect between the matrix and the ceramic. Some difficulties still exist for this process such as agglomeration, settling of particulates, segregation of secondary phases, interfacial reactions, and particulate fracture during mechanical agitation.

In the spray deposition process, the reinforcement particulates are introduced into the stream of molten alloy which is subsequently atomized by jets of inert gas. The sprayed mixture is collected on a substrate in the form of a reinforced metal matrix billet. This process combines the blending and consolidation steps of the powder metallurgy process and thus promises major saving in MMC production.

**Continuous reinforcement**

The most commonly used continuous fibres in MMCs include graphite fibres, boron fibres and silicon carbide fibre (Lee and Mykkanen, 1987). Graphite fibres are manufactured by treating an organic base material fibre (precursor) with heat and tension, leaving a highly ordered carbon structure. Boron and silicon carbide fibres are made by chemical deposition from vapour onto a tungsten or carbon filament substrate.

Silicon carbide fibres have high temperature stability and low cost, and they have become desirable components of advanced metal matrix composites. Two types of SiC based fibre, the SCS series with carbon core and sigma with tungsten core, are available in single fibre form (Upadhyaya, 1995). Each of the two types fibre is produced by chemical vapour deposition. In the fabrication process of silicon carbide fibres, the carbon or tungsten core is heated electrically and pulled continuously through a deposition tube. Different gas mixtures whose main components are chlorosilane (e.g. CH$_3$SiCl$_3$, (CH$_3$)$_2$SiCl$_2$, or CH$_3$SiHCl$_2$), hydrogen and alkane hydrocarbons are introduced into the tube. Change in the concentration of the gases or in the deposition temperature produces different microstructure in the deposited SiC. Carbon and silicon coating is used on the outside which is more stable in contact with molten metal.
Methods for fabrication of continuously reinforced composites must satisfy the following: 1) achieve fibre alignment and uniform distribution, 2) avoid fibre damage, 3) avoid interfacial reactions. There are three fabrication methods: 1) The powder cloth method, in which the prealloyed powder, binder and wetting agent are stacked in alternating layers with fibre mats and consolidated in a vacuum hot-press. 2) The foil-fibre-foil method which is similar to the powder cloth method, but matrix material foil is used instead of powder sheets. 3) The fibre precoating method, in which fibres are precoated with matrix alloys by using spraying or physical vapour deposition, and the composites are formed by vacuum hot pressing.

The metal matrix composite materials have distinguished mechanical properties, but the corrosion-resistance of MMCs is a very important factor to make the materials suitable for wide-scale practical use. Since the work in this thesis is concerned with the corrosion performance of silicon carbide reinforced aluminium MMCs, the following sections will focus on the work of other researchers concerning the corrosion properties of aluminium alloy and aluminium MMCs.

### 2.2 CORROSION PROPERTIES OF ALUMINIUM AND ALUMINIUM ALLOYS

Aluminium is a thermodynamically reactive metal because of its high position in the electrochemical series. It is thus somewhat surprising that aluminium and its alloys are relatively stable in most environments. The reason for such high resistance to attack is the oxide film provided to Al by nature. The rapid formation of an oxide film bonded strongly to the aluminium surface inhibits the bulk reaction predicted from thermodynamic data. Although this film is extremely thin and easily damaged, it has remarkable self-healing properties to re-form immediately in most environments if it is damaged.
2.2.1 Oxide Film

Kaesche (1978) has concluded that there are three distinctly different conditions of surface oxidation: 1) nonanodized aluminium carrying an air-formed oxide film, 2) barrier-type anodized aluminium with nonporous oxide, 3) porous-type anodized aluminium.

A number of investigators have demonstrated that the oxide film formed on Al in normal atmospheres grows to thicknesses much greater than 1nm (10Å) and continues to grow at a decreasing rate for several years to reach a thickness of some tens of nanometres. The rate of film growth becomes more rapid at higher temperatures and higher relative humidities. Hunter and Fowle (1956) believe that naturally and thermally formed films on aluminium consist of two layers, a layer of compact barrier-type oxide next to the metal and an outer layer of more permeable oxide. The barrier layer is formed by the simple combination of aluminium and oxygen and the thickness is controlled by temperature alone. At low temperature, the air-formed barrier layer is about 10Å. The thickness of the outer porous layer is determined by time and natural processes associated with the particular environment.

Much thicker surface oxide films, that give enhanced corrosion resistance to aluminium and its alloys, can be produced by various chemical and electrochemical treatments. Barrier-type, anodized aluminium is obtained by treatment in electrolytes which do not dissolve Al(OH)_3 and is expected to produce essentially nonporous oxide. The thickness is several hundred nanometres. Porous-type anodized aluminium is obtained by treatment in electrolytes such as sulphuric acid, which dissolve Al(OH)_3 but at a low rate. It gives a structure of a thin barrier-type oxide topped by a porous oxide which is easily grown to 10 or 20 μm.

Metzger and Zahav (1978) drew schematic maps about the breakdown-pitting repair event in a porous anodic film (Figure 2.4). A breakdown leads to initiation of a pit, the pitting is presumed unstable and the pit surface is reanodized. The
transient pitting accompanies stable film growth.

By convention, the property of 'passivity' is assigned to nonanodized aluminium, meaning aluminium carrying the air-formed film only, and immersed in approximately neutral, noncomplexing solutions. Kaeshe (1978) considered that either thin passive film or thick nonreactive film had very similar composition and both were insulators which block the passage of both ions and electrons. This is in contrast to the oxide film of, say, iron-nickel-chromium alloys which are semiconductors.

2.2.2 Uniform Dissolution of Passive Film

The conditions for thermodynamic stability of aluminium in pure water are expressed by the Pourbaix (potential versus pH) diagram shown in Figure 2.5. Two
Figure 2.5 Pourbaix diagram for aluminium (After Deltombe et al, 1966).

Sloping lines, a and b, in this diagram express the following reactions:

\[ \text{H}^+(aq) + e(M) = \frac{1}{2} \text{H}_2(g) \]

\[ E_{\text{H}_2} = 0.00 - 0.059\text{pH} \text{ V, SHE at } 25^\circ\text{C} \text{ 1atm} \]

and

\[ \frac{1}{2} \text{O}_2(g) + \text{H}_2\text{O}(l) + 2e(M) = 2\text{OH}^-(aq) \]

\[ E_{\text{O}_2} = 1.23 - 0.059\text{pH} \text{ V, SHE at } 25^\circ\text{C} \text{ 1atm} \]

respectively. Water will decompose to oxygen above the line b and decompose to hydrogen below the line a. Aluminium is a highly active metal, the immune domain is located far lower than line a. Fortunately, in non-complexing solutions of pH
roughly between 4 and 9, aluminium tends to become covered with a film of oxide to give a passive domain. The limits of this range vary with different conditions.

In acid or alkaline solutions, the aluminium will be attacked as soon as the oxide film is eliminated. This dissolution is slower in acid solution than in alkaline solutions. Aluminium is filmed by hydroxide even during rapid dissolution in alkaline solutions. The overall reaction of uniform corrosion of aluminium is

$$\text{Al} + \text{OH}^- + 3\text{H}_2\text{O} = \text{Al(OH)}_4^- + 3/2\text{H}_2$$

Kaesche (1978) concluded that the rate of film dissolution is governed by $\text{OH}^-$ diffusion. Furthermore, in the presence of sufficiently acid solutions, passive film is not stable and is rapidly dissolved. Aluminium then decomposes water with the evolution of hydrogen, and dissolves as trivalent $\text{Al}^{3+}$. The chemical reaction can be expressed as following:

$$2\text{Al} + 6\text{H}_2\text{O}^+ = 2\text{Al}^{3+} + 3\text{H}_2 + 6\text{H}_2\text{O}.$$  

In neutral solutions, oxide film is not stable under certain conditions. For example, the corrosion rate of aluminium is increased in fluoride solutions (Pryor 1958). The solubility of aluminium oxide is much larger in fluoride solutions than in chloride solutions (Lorking and Mayne 1966). One explanation is that fluoride solution can dissolve the air-formed oxide film due to the formation of complex ions such as $\text{AlF}^{2+}$ to $\text{AlF}_6^{3-}$. Kaesche (1974) has measured the corrosion rate of aluminium in aerated fluoride and chloride solutions. The rate in fluoride solution is 20 g/m² in 4 weeks, giving evenly etched specimens, whereas it is essentially zero in aerated chloride solutions, giving specimens with some pits.

### 2.2.3 Pitting Corrosion

As shown in the Pourbaix Diagram (Figure 2.5), aluminium is in a passive condition
in nearly neutral solutions. This kind of environments is the situation in which aluminium or aluminium based alloy is normally used. Unfortunately, pitting occurs commonly on aluminium which has a protective surface film, and it causes more failures and requires more expensive repairs than thinning of the metal by uniform corrosion.

The tendency of pitting corrosion

The tendency of a metal or alloy toward pitting can be estimated by 1) determination of the breakdown potential $E_b$, 2) determination of the minimum concentration of Cl$^-$ ions in solution causing pitting, and 3) measurement of the number and, eventually, the depth and width of pits in a suitable standard solution. The last two methods are used to observe pitting directly by changing the concentration of Cl$^-$ ions, counting the pits or measuring their greatest depth at a constant potential.

![Idealised anodic polarisation curve for system exhibiting passivity.](image)

Figure 2.6 Idealised anodic polarisation curve for system exhibiting passivity.

A idealised anodic polarisation curve for a system exhibiting passivity is shown in Figure 2.6, where $E_b$ is the breakdown potential, $E_p$ is the passivation potential, $i_p$ is the passive current density, $i_c$ is the critical current density for passivation, and $E_c$ is the corrosion potential. The breakdown potential, $E_b$, is sometimes referred to as the pitting potential. Some authors make a further distinction between that
potential which will initiate pits on a pit-free surface and the potential required to activate pits already present. Below $E_p$, at more negative potentials, the metal is in the passive state, and above $E_p$, pitting corrosion occurs, i.e., passive and active states coexist on the surface of the metal. The more positive $E_p$, the higher resistance is the alloy to pitting.

The potential to which the aluminium is polarized by a specific cathode reaction determines corrosion current density and corrosion rate. For aluminium, pitting corrosion is most commonly produced in aerated halide solutions. In the presence of oxygen, the metal is readily polarized to its pitting potential. On the other hand, aluminium does not develop pitting in aerated solutions of most non-halide salts because its pitting potential in these solutions is considerably more noble than in halide solutions, and it is not polarized to these potentials in normal service.

Many authors have compared $E_h$ values obtained using various methods: potentiostatic, potentiokinetic, galvanostatic, and chemical approach. Some of them found a very good relationship between $E_h$ values obtained by all above methods. On the contrary, inconsistent results are also observed by some investigators. In general, the correct results of $E_h$ can be obtained by the point to point potentiostatic method at the condition when induction time for pit nucleation is not long. The correct value of $E_h$ can also be obtained by using the galvanostatic method.

**Electrolyte composition**

Pitting of aluminium is well known to occur in solutions containing chloride, bromide, or iodide as one of the anionic species, the rather large anions such as $\text{ClO}_4^-$, $\text{NO}_3^-$, $\text{SCN}^-$ also act as pit promoters. Pitting can also be found in perchlorate, thiocyanate and nitrate solutions. Weng and Huo (1988) proposed three possible effects of chloride ions on localized corrosion of aluminium: 1) initiated localised corrosion; 2) accelerated local anodic dissolution; and 3) impeded repassivation.
Metzer and Zahavi (1978) used transmission electron microscopy to observe the film which is detached from 99.999% aluminium anodized in 2.4 M H₂SO₄ with and without Cl⁻ at 5 mA/cm². They deduced from their results that the role of chloride was not to produce film breakdown, which occurred in its absence. It also had no apparent direct effect on film growth. Its role was then in the stabilization of pit growth. The effect of Cl⁻ was statistically to tend to increase the lifetimes of the transient pits.

Sites most susceptible to pitting

The resistance of the metal to pitting is related to the homogeneity of the surface. In practice, surface films are heterogeneous. A number of flaws occur in the film where it is less thick, less strong or more permeable than elsewhere. Pryor and Keir (1955) gave evidence for the presence of isolated flaws. They treated the cold rolled aluminium, covered with an air-formed oxide film, by cathodic polarization in 1M NaCl solution containing 0.1% CuSO₄ at a current of 1 µA/cm² for 2 min and found that the copper deposition occurred on isolated spots only. The result means that the electronic resistance of the air-formed oxide film on aluminium is so high that it prevents the migration of electrons to the film/solution interface except at small 'weak' points of low electronic resistance.

Since these flaws exist in the surface film, the aluminium may start dissolving at these sensitive points when it is immersed in an electrolyte. After that, one of the following cases may happen: 1) the film is repaired again at the pores; 2) localised corrosion continues at the exposed bare metal, or 3) breakdown extends sideways from the pore until there is no film left.

Due to the limitation of solid solubility of most other elements in aluminium at room temperature, either the presence of other elements in aluminium as impurities or as deliberate alloying additions increases its susceptibility to pitting. The reason for this behaviour lies in the intrinsically high chemical reactivity of aluminium, so that aluminium will be anodic to most second-phase intermetallic particles. Bond et al (1966) investigated the micro-segregation of the
dominant residual impurities: Fe, Cu, and Si, and found segregation caused the
decrease of cathodic overvoltage and corrosion potential displacement in the
potential region where pitting occurs. The authors suppose that distribution rather
than the total amount of residual impurity is more important in producing a
tendency for pitting. In addition, the second-phase intermetallic particles provide
phase boundaries, which can also contribute to pit effects.

Ives (1992) concludes that there four pit nucleation processes associated with
inclusions as shown in Figure 2.7. In type one, the inclusion is active. Type two is
related to multiphase inclusions, certain phase(s) are preferentially dissolved. Both
type one and two represent the situations where the inclusion acts anodically with
respect to metal matrix. In type three, the matrix in the vicinity of an inclusion
which is electrochemically cathodic to the matrix is preferentially dissolved. Type
four is the disbonding at the interface between matrix or inclusion.

Excepting the intermetallic particles or nonmetallic inclusions, some other positions are also be considered as susceptible sites for pits corrosion such as grain boundaries, local scratches or abrasions, differential strain, and dislocations.

**Mechanism**

Considering the mechanism of pitting corrosion, two stages may be distinguished: 1) nucleation of pits on the passivated metal surface and 2) development of the pits. Unfortunately, no universally accepted mechanism is available after more than half a century of work. Kruger (1988) classified three groups of model for initiation: 1) ion migration or penetration, 2) adsorbed ion displacement, and 3) breakdown of repair. The most popular accepted mechanism of pitting corrosion for aluminium is the ion migration or penetration model.

The main ideas for ion migration or penetration models are that damaging anions move through the passive film, and the breakdown process is completed when an anion reaches the metal/film interface. The different migratory ways form different models. The pore mechanism states that the existence of pores or defects in the film allows instantaneous penetration and hence the instant initiation of localised corrosion. The other types of penetration model are those models involving migration of the damaging anion through a lattice, defects, or some sort of ion exchange process.

Szklarska-Smialowska (1992) believes that the existence of defects on the metal surface is a necessary condition for pit nucleation. She argues that since the aluminium oxide film is not an effective obstacle for penetration of chloride ions and water to the metal surface, the penetration of chloride ions to the metal is not the rate determining step in pitting corrosion. The rate determining step for stable pit growth is the establishment of a solution composition within the pre-existing defect at the metal/film interface that allows active dissolution of the metal.
Another approach, which is made by Rais and Dalard (1987), is based on point defect analysis in aluminium oxide. Their idea is as follows. During potentiostatic oxidation, $\text{Al}^{3+}$ formed at the metal/oxide interface migrate to the oxide/electrolyte interface. This cation migration is the main process governing the passivity breakdown. The local electrical properties of the oxide are modified by Cl$^-$ adsorption at the oxide/electrolyte interface. This anion can form a soluble Al salt responsible for the dissolution of Al. Therefore, a current develops leading to the oxidation of Al at the metal/oxide interface and to a local destruction of the oxide, followed by pitting.

Szklarska-Smialowska (1992) concluded that pits could develop in chloride solutions only when acidic conditions were established within pits. Some authors believed that a necessary condition for stable pit growth was the presence of a salt film at the pit bottom. Pit propagation in Al was usually reported to be diffusion controlled (Scully 1991, Frankel 1990, Hunkeler and Bohni 1981). Hunkeler and Bohni investigated the effect of additional foreign ions, they observed that the pit growth rate was directly controlled by the conductivity of the surrounding electrolyte. This indicated the importance of the ohmic potential drop for pit growth. Corrosion tunnelling was the general mode of pit propagation of aluminium in chloride media, irrespective of the macroscopic aspect of the attack (Edeleanu 1960, Baumgärtner and Keasche 1990). Pickering and Frankenthal (1972) considered that the bottom of pit was electrochemically active. Within the

![Figure 2.8 Schematical representation of pit shapes.](image-url)
tunnel, ion movement was governed by diffusion and migration.

Pits can be schematically represented by hemi-spheres of radius r, and tunnels by constant diameter cylinders of length d. Both r and d have been observed to vary with time according to a $kt^a$ law, where t is time, k and $a$ are constants depending on experimental conditions. A similar expression holds for current but with a different exponent, i=$kt^b$.

### 2.2.4 The Behaviour of Various Types of Aluminium Alloy

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Nominal composition, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>0.12 Cu - 99.00 Al (min)</td>
</tr>
<tr>
<td>2014</td>
<td>Al - 0.8 Si - 4.4 Cu - 0.8 Mn - 0.5 Mg</td>
</tr>
<tr>
<td>2124</td>
<td></td>
</tr>
<tr>
<td>3003</td>
<td>Al - 0.12 Cu - 1.2 Mn</td>
</tr>
<tr>
<td>4032</td>
<td></td>
</tr>
<tr>
<td>5052</td>
<td>Al - 2.5 Mg - 0.25 Cr</td>
</tr>
<tr>
<td>6061</td>
<td>Al - 0.6 Si - 0.27 Cu - 1.0 Mg - 0.2 Cr</td>
</tr>
<tr>
<td>6063</td>
<td>Al - 0.4 Si - 0.7 Mg</td>
</tr>
<tr>
<td>7072</td>
<td>Al - 1.0 Zn</td>
</tr>
</tbody>
</table>

In order to get a special structure property, some alloying elements are added into
aluminium to form different property aluminium alloys. The common aluminium alloys are given in Table 2.2. The alloying elements are normally not distributed
Some kind of second-phase particulates are formed, which is one of the factors necessary to introduce pitting corrosion due to their differing electrode potentials with the matrix. The possible phases in some aluminium alloys are listed in Table 2.3 and the electrode potentials of some second-phase constituents in aluminium alloys are listed in Table 2.4. The compositions of Al alloys in Table 2.2 and Table 2.3 have differences, this is because Fe and Si are not alloying elements, but they exist in most aluminium alloys as impurities.

Table 2.4. Electrode Potentials of Aluminium Solid Solutions and Constituents
(after Metal Handbook, 1987)

<table>
<thead>
<tr>
<th>solid solution or constituent</th>
<th>potential V(a)</th>
<th>solid solution or constituent</th>
<th>potential V(a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg₆Al₈</td>
<td>-1.24</td>
<td>Mn₄Al₃</td>
<td>-0.85</td>
</tr>
<tr>
<td>Mg₂Al₃</td>
<td>-1.24</td>
<td>99.95 Al</td>
<td>-0.85</td>
</tr>
<tr>
<td>Al+4MgZn₂(b)</td>
<td>-1.07</td>
<td>Al+1Mg₂Si(b)</td>
<td>-0.83</td>
</tr>
<tr>
<td>Al+4Zn(b)</td>
<td>-1.05</td>
<td>Al+1Si(b)</td>
<td>-0.81</td>
</tr>
<tr>
<td>MgZn₂</td>
<td>-1.05</td>
<td>Al+2Cu(b)</td>
<td>-0.75</td>
</tr>
<tr>
<td>CuMgAl₂</td>
<td>-1.00</td>
<td>CuAl₂</td>
<td>-0.73</td>
</tr>
<tr>
<td>Al+1Zn(b)</td>
<td>-0.96</td>
<td>Al+4Cu(b)</td>
<td>-0.69</td>
</tr>
<tr>
<td>Al+7Mg(b)</td>
<td>-0.89</td>
<td>FeAl₃</td>
<td>-0.56</td>
</tr>
<tr>
<td>Al+5Mg(b)</td>
<td>-0.88</td>
<td>NiAl₃</td>
<td>-0.52</td>
</tr>
<tr>
<td>Al+3Mg(b)</td>
<td>-0.87</td>
<td>Si</td>
<td>-0.26</td>
</tr>
</tbody>
</table>

(a) 0.1N calomel scale, measured in an aqueous solution of 53 g per litre NaCl + 3 g per litre H₂O₂ at 25°C.

(b) Solid solution
The various aluminium alloys have differing corrosion resistance because of the different phases found in them. Many books concerned with aluminium alloys have set out the properties of each type of alloy (Metal handbook 1987, Godard et al 1967, and American Society for Metals). The following paragraphs will briefly list the effect of composition and microstructure on the corrosion of aluminium alloys.

Aluminium-copper alloys were the first heat-treatable, high-strength aluminium-base materials and have been used for more than 80 years in structural applications, particularly in aircraft and aerospace applications. Although the electrode potential of Al-Cu alloys increases with the amount of copper in solid solution, these kind of alloys have relatively poor corrosion resistance, and require surface protection when used in corrosive environments. There are three factors which affect the corrosion resistance. 1) Copper can increase the conductivity of the surface film, leading to loss of the protective effect of the passive film. 2) As corrosion progresses, copper ions, which initially dissolve into solution, replate onto the alloy to form metallic copper cathodes. Reduction of copper ions and increased efficiency of $\text{O}_2$ and $\text{H}^+$ reduction reactions in the presence of copper increases the corrosion rate. 3) The precipitate phase CuAl$_2$ likes to concentrate in the grain boundaries and gives rise to a high degree of susceptibility to intergranular corrosion and stress corrosion.

Aluminium-manganese alloys have very high resistance to corrosion. They are widely used for cooking and food processing equipment, chemical equipment, and various architectural products requiring high resistance to corrosion. Manganese and aluminium form a compound that has almost the same electrode potential as the aluminium matrix. Further, MnAl$_6$ can absorb some iron in solid solution and some manganese can also be taken in solid solution into FeAl$_3$, with the result that the detrimental effect of the iron constituent on the corrosion resistance is reduced.

Elemental silicon is present as second-phase constituent particles in aluminium-silicon alloys. It is cathodic to the aluminium solid solution by several hundred millivolts. However, the effect of silicon on the corrosion resistance of these alloys is minimal because of a low corrosion current density resulting from the fact that
the silicon particles are highly polarized. Silicon in solid solution has little effect on the electrode potential of aluminium, so aluminium - silicon alloys are corrosion resistant.

In aluminium - magnesium alloys, the solid solution is more anodic than aluminium. $\text{Al}_8\text{Mg}_5$ particles are normally formed, which are strongly anodic to the matrix. When it is present in a continuous network form it leads to susceptibility to intergranular corrosion and stress corrosion. If $\text{Al}_8\text{Mg}_5$ particles are dispersed uniformly throughout the matrix, alloys are generally as resistant to corrosion as commercially pure aluminium, and they are more resistant to salt water and some alkaline solutions.

When magnesium and silicon are both present, a stoichiometric second phase constituent, magnesium silicide ($\text{Mg}_2\text{Si}$) is formed. The electrode potential of $\text{Mg}_2\text{Si}$ is essentially the same as the potential of aluminium. In general, alloys with balanced magnesium and silicon contents in correct proportion to form $\text{Mg}_2\text{Si}$ (as for AA-6061) have slightly better corrosion resistance than unbalanced alloys.

In solid solution, zinc increases the electrode potential of aluminium substantially. As a result, Aluminium - zinc alloys are widely used as alclad coatings on aluminium alloys, and as galvanic anodes in sea water for cathodic protection of steel ship hulls, ballast tanks, and offshore oil - field structures.

2.3 CORROSION PROPERTY OF MMCS

In recent years, extensive work has been done on the development of metal matrix composites for their enhanced physical and mechanical properties, but there are relatively few investigative studies addressing their corrosion behaviour. In general the duplex phase structure will encounter more serious localised attack compared
to their monolithic matrix alloy. One of the potential problems is the galvanic coupling between reinforcing materials and the metal matrix. Structure defects could also result in increasing localised corrosion of the matrix. Rapid corrosion would not only limit service lifetimes, but also affect the mechanical or physical properties for which the composite is designed. For example, interfacial corrosion of a fibre/metal composite would be expected to result in a decrease in transverse load-bearing capability (Trzaskoma, 1991).

2.3.1 SiC/Al Metal Matrix Composites

The traditional methods for evaluating the corrosion resistance of MMC as compared with matrix alloy are measuring the weight lost through exposure to aggressive solutions, but these methods are not suitable for estimating the pitting rate. Electrochemical methods are useful tools for assessment of pitting potential, corrosion potential and corrosion current. Now scanning electron microscopy (SEM) is more often used to detect the pit number and pit shape on different specimens.

In Metzger and Fishman's review paper (1983), three groups of investigators' works were cited on the corrosion of SiC reinforced MMCs, and two of them were unpublished research. DeJarnette and Crowe in 1982 compared 20 vol% SiC/2024 Al with commercial extruded Al 2024-T4 as immersed in 3.5% NaCl. They found that the corrosion rates were similar in deaerated solutions; while the composites were corroding about 40% faster during a four-week exposure in aerated solutions. Lore and Wolf in 1981, with SiC/6061 Al, over the range 0 to 30 vol% SiC, found little difference in rates of weight loss in 3.5% NaCl. Both groups of investigators noted that pits initiated at SiC particles.

Trzaskoma et al (1983) conducted anodic polarization studies in 0.1 M NaCl of Al 2024, 5456 and 6061 composites with 20 vol% SiC (whiskers of diameter 0.5-1.0 μm and length up to 50 μm) prepared by the powder metallurgy technique and their
matrix alloys. Samples were mounted in epoxy, abraded through 600 grit paper, rinsed with water, air dried, and stored in desiccator until used. $E_{\text{corr}}$ was recorded by immersing samples in solution for approximately 2 hr until steady; at this time, the potential was increased in 10 mV intervals and the steady current recorded (usually after 10 min). The potential at which the current continuously increased was interpreted to be the $E_{\text{pit}}$. The results (Table 2.5) showed that the SiC phase did not affect the susceptibility to pit initiation of the composites tested, except for Al 2024, and in the deaerated solutions, $E_{\text{corr}}$ for all samples, was several hundred millivolts negative to the values found for solutions containing oxygen. Pitting potentials were independent of the presence of oxygen in 0.1 N NaCl for all alloys and composites studied. After pitting in deaerated 0.1 N NaCl at -0.610 mV for 30 min, they found that pits on the composite differed in size and structure from those on the base alloy. Small rounded shallow pits developed on the alloy. They also found that general corrosion was most significantly affected by the presence of oxygen rather than by the alloy type or SiC phase. The corrosion rate for all specimens was significantly lower in deaerated solutions.

Table 2.5 Open-circuit potentials ($E_{\text{corr}}$) and pitting potentials ($E_{\text{pit}}$) (vs. SEC) in 0.1N NaCl solutions (Trzaskoma et al, 1983)

<table>
<thead>
<tr>
<th>Materials</th>
<th>Open to the air</th>
<th>Deaerated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{\text{corr}}$</td>
<td>$E_{\text{pit}}$</td>
</tr>
<tr>
<td>2024</td>
<td>-0.546</td>
<td>-0.540</td>
</tr>
<tr>
<td>SiC/Al 2024</td>
<td>-0.652</td>
<td>-0.640</td>
</tr>
<tr>
<td>5456</td>
<td>-0.704</td>
<td>-0.690</td>
</tr>
<tr>
<td>SiC/Al 5456</td>
<td>-0.705</td>
<td>-0.695</td>
</tr>
<tr>
<td>6061</td>
<td>-0.683</td>
<td>-0.673</td>
</tr>
<tr>
<td>SiC/Al 6061</td>
<td>-0.669</td>
<td>-0.660</td>
</tr>
</tbody>
</table>
Most results from different investigators indicate that SiC reinforced aluminium matrix composites are more susceptible to corrosion attack than the matrix alloy (Turnbull 1992, Metzger and Fishman 1983). To explain this phenomena, some different conclusions have arisen as described in the following sections.

![Potential at the cathodic current density equal to 32 \( \mu m/cm^2 \) (Roepstorff and Maahn, 1992).](image)

**Figure 2.9** Potential at the cathodic current density equal to 32 \( \mu m/cm^2 \) (Roepstorff and Maahn, 1992).

**Galvanic cell formed by SiC and Al**

Roepstorff and Maahn (1992) examined materials containing 0.5-10-20 vol% SiC/Al composites. One series was produced by conventional mixing of the Al and SiC powders, and another series was produced from SiC powder which was coated by a special process. Based on weight loss measurements, there was a tendency to some beneficial effect from the coating process. In the meantime, the potential at a cathodic current density of 32 \( \mu m/cm^2 \) had been measured (Table 2.6) according to Figure 2.9. They found the presence of silicon carbide in an aluminium matrix increased the activity of oxygen reduction. It was assumed that the increase in activity was solely connected to the silicon carbide, which meant that the oxygen reduction in practice would be located on the surface of the silicon carbide particles. Based on this result and microscopic observation, they concluded that SiC particles operated as local cathodes and increased the oxygen reduction rate:
The locally produced hydroxyl ions gave rise to an increase in the pH-value of the environment near the particles. This change in pH was a destabilizing factor for the passive film on the aluminium.

Table 2.6 Potential (mV SCE) at a cathodic current density of 32 μA/cm²
(Roepstorff and Maahn 1992)

<table>
<thead>
<tr>
<th>% SiC</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>uncoated</td>
<td>-1215</td>
<td>-747</td>
<td>-759</td>
<td>-709</td>
</tr>
<tr>
<td>coated</td>
<td>-1200</td>
<td>-810</td>
<td>-720</td>
<td>-633</td>
</tr>
</tbody>
</table>

Galvanic cell formed by intermetallic and aluminium

In Trzaskoma’s recent work (1989, 1990), pit morphology of Al 5456, Al 6061, SiC₆₀/Al 5456 and SiC₆₀/Al 6061 was studied by using electrochemical procedures, EDX (electron dispersive X-ray) analysis and SEM (scanning electron microscopy) analysis. The reasons for a significantly greater number of pits formed on the composites than on the corresponding alloys were given. According to the experiments results, the author suggested that the SiC was not a necessary factor involved in the nucleation of pits. Pits were however associated with micro-particles within the metal matrix. In the cases of Al 5456 and SiC₆₀/Al 5456 these particles were intermetallic phases composed of alloying elements Mg, Cr, Mn, Al and the impurity Fe. The composition of micro-particles in fresh pits had been determined by EDX analysis. A fresh pit was formed around a micro-particle as shown in SEM photographs (Figure 2.10). Under equivalent conditions of preparation and
processing, a greater number of intermetallic phases formed in the composite than the alloy and hence more pits initiated on the composite material. The smaller size of the SiC reinforcement might interfere with or decrease the metal dissolution rate. McIntyre et al (1987) also mentioned that intermetallics strongly influenced corrosion in their report.

Figure 2.10 (a). Typical fresh pits on wrought Al 5456. (b) Typical fresh pits on SiC/Al 6061.

A double cyclic polarisation technique combined with a long-term immersion test was used to study the corrosion behaviour of SiC/Al, SiC/357 Al and their matrix alloys. Otani, McEnaney and Scott (1988, 1989) found no evidence to show that the corrosion of aluminium and its alloys was accelerated by the presence of SiC fibres. The microstructure and composition of the metal matrix had a major influence on the corrosion behaviour of the MMCs. In Al based composites, Fe introduced as an impurity during fabrication formed FeAl$_6$ compound and tended
to segregate at the interface between the fibre and the matrix and at grain boundaries (Figure 2.11). The presence of a large quantity of a second phase such as FeAl₆ produced a strong micro-galvanic corrosion effect due to its much more positive corrosion potential. The difference of corrosion potential between aluminium (-0.85 V) and FeAl₆ (close to -0.56V) was mentioned. They also raised the possibility that when sufficient silicon was present in 357 alloy, it could form FeSiAl₅ rather than FeAl₆ and that this ternary phase was not severely attacked. There was an indication too that 357 alloy (Al-Si-Mg) with its Al-Si eutectic segregation suffered greater attack than metal containing iron and silicon together. That was because, in Al-Si alloy based composites, Si tended to segregate at the fibre/matrix interface, and micro-galvanic corrosion between Al matrix and Si could...
happen. The effect of fibres on corrosion was secondary, by acting as physical barriers to pit propagation. They suggested that when choosing MMC systems for use in corrosive environments a matrix alloy should be adopted which contained elements such as magnesium or zinc with a more negative corrosion potential in order to reduce localised attack on any second phases present.

Modi et al (1992) were interested in the corrosion behaviour of squeeze-cast aluminium alloy-silicon carbide composites. The materials they used were Al-4.5Cu-0.12Fe alloy and reinforced with SiC particles (10-15 μm) and fibres (length 3mm and diameter 10-15 μm). The corrosion experiments, such as general immersion, erosion-corrosion and potentiodynamic polarization, were performed in 3.5% NaCl solution in atmospheric conditions. An increased corrosion rate for composite materials was found from the general immersion test, in addition pitting and attack at the CuAl₂ precipitate-Al interface and dispersoid-matrix interface were found. Their conclusion was that the dispersoid-matrix interface played a dominant role in enhancing the rate of material loss of the composites.

<table>
<thead>
<tr>
<th>Material</th>
<th>Mean area fraction (%)</th>
<th>Standard deviation (%)</th>
<th>Average particle size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6061 Al</td>
<td>0.40</td>
<td>0.28</td>
<td>0.75</td>
</tr>
<tr>
<td>15 wt% SiCₚ/6061 Al (BP)</td>
<td>0.32</td>
<td>0.09</td>
<td>0.75</td>
</tr>
<tr>
<td>20 wt% SiCₚ/6061 Al</td>
<td>0.86</td>
<td>0.25</td>
<td>1.00</td>
</tr>
<tr>
<td>30 wt% SiCₚ/6061 Al</td>
<td>0.76</td>
<td>0.18</td>
<td>1.25</td>
</tr>
</tbody>
</table>
The polarisation behaviour of SiC/6061 Al MMCs was investigated by Griffiths and Turnbull (1994). Al alloy 6061 and Al alloy 6061 reinforced with 20 wt% 13 μm SiC particles (NEL/NPL), 15 wt% and 30 wt% 10 μm SiC particles (BP) were used in their works. The area fraction of intermetallic precipitates were examined through backscattered electron imaging and is listed in Table 2.7. Comparison of SiC and Al alloy (Figure 2.12 and Figure 2.13) shows that they can support similar cathodic current densities, therefore there is no basis for significant galvanic interaction between the SiC and the matrix alloy in the MMC. Increased cathodic current density was found on 20 wt% SiC/6061 Al as compared with 6061 Al in aerated stirred 3.5 wt% NaCl solution, the authors attributed this phenomenon to the increased area fraction of intermetallic precipitates rather than the SiC content directly. This is quite different from the explanation of Roepstorff and Maahn as mentioned before even though the experimental results were similar. Another phenomenon they found was that the effect of SiC reinforcement on the cathodic polarisation behaviour of 6061 Al in de-aerated, stirred 3.5 wt% NaCl solution was
dependent on the pH. This was concluded to be due to the differences in the characteristic of the surface film in relation to the presence of SiC.

Other explanations
H. Sun et al (1991) studied the corrosion behaviour of materials consisting of 6061-T6 Al alloy reinforced with 15 to 40% SiC particles. The SiC particles were a mixture of the moissainite and β-phase structures. Electrochemical tests were done in different concentrations of NaCl solutions that were open to air, aerated, or deaerated. They found that there was no clear relation between the corrosion potentials and the volume fraction of SiC, but the degree of corrosion in NaCl solutions increased with increasing SiC contents. They did not fully agree with Trzaskoma’s opinion that pits initiated at intermetallic particles. Their evidence was that a higher volume percentage of intermetallic particles, Mg₂Si, was found.
in 20 vol% SiC/6061 Al, but no more pits were observed in this composite. The surface films were considered to be the dominate factor, film breakdown was related to the volume percentage of SiC particle and to the NaCl concentration.

Aylor et al (1983, 1985) studied the pitting behaviour of SiC\textsubscript{w}/6061 Al, 6061 Al, SiC\textsubscript{w}/6061-T6 Al (fabricated by powder metallurgy) and wrought 6061-T6 Al in ASTM ocean water. The volume fraction of SiC was 25\% and the whiskers were approximately 0.1 to several microns in diameter and 1-50 μm in length. Through electrochemical testing (including \(E_{corr}\) monitoring, cyclic anodic polarization, and potentiostatic holds), they obtained similar results to Trzaskoma. The presence of SiC in 6061 Al matrix did not alter the corrosion potential in aerated ocean water, and the SiC did not increase the pitting susceptibility of the SiC/Al composite. The morphology and extent of pitting differed between SiC/Al and Al materials. The pits were greater in number, smaller in size, and more shallow in penetration depth relative to the un-reinforced aluminium alloys. Marine exposure methods combined with SEM analysis were also used in their works. It was found that pitting corrosion was concentrated around the SiC whiskers. The authors suggested that the crevices formed at each SiC-Al interface were preferential sites for pitting corrosion.

Nishimura et al (1991) investigated two kind of SiC\textsubscript{w}/Al MMC, i.e. SiC\textsubscript{w}/6061 Al and SiC\textsubscript{w}/7075 Al, which were manufactured by using the squeeze casting method. Through the TEM, they found that a reaction phase was formed between SiC\textsubscript{w} and 6061 Al matrix. This interfacial layer appeared to decrease the cathodic overpotential of hydrogen evolution in 6061 MMC in deaerated 3.5\% NaCl solution. In SiC\textsubscript{w}/7075 Al, no reaction phase was found at SiC\textsubscript{w}/7075 Al interface when it was aged at 110\(^\circ\)C. The coagulated precipitates were found at the grain boundary in metal matrix of 170\(^\circ\)C aged 7075 MMC. They considered that the growth of these precipitates along the grain boundary could improve the localized corrosion resistance.

Pitting potentials, repassivation potentials, and induction times for pit initiation on
SiCw/AA6061, AA6061 and pure Al in a sodium borate/boric acid electrolyte (pH 7.2 and 8.4) containing 0.1 N [Cl] were measured by Golledge et al. (1989). Pure (99.99) Al samples were cut from 20 mm rod, wrought AA6061 and SiCw/AA6061 (20 v/o reinforcement) were cut from 1/4" plate and an extruded bar. The alloy and MMC were given T-6 heat treatments. The results showed that the pitting potentials for SiC/AA6061 and AA6061 were similar to the result of Trzaskoma and Aylor et al. That means the tendency to pit is not increased by the SiC reinforcement. By using induction time and ellipsometry (after immersion at open circuit for 1 hour in a chloride-free solution), they found that the kinetics of pit initiation were different on the MMC and the wrought alloy. The authors attributed this to the oxide film. The oxide formed on the MMC was less dense, therefore it was less resistant to diffusion of chloride ions. Further, as oxide growth on aluminium proceeded by both anion ingress and cation egress, SiC whiskers should be expected to be incorporated bodily into the oxide as it grows, which might affect defect structure and otherwise render the oxide less resistant to breakdown.

Table 2.8 Heat treatments for PM SiCp/Al alloy MMC and MA-87 alloy (Paciej and Agarwala, 1988).

<table>
<thead>
<tr>
<th>Material Temper</th>
<th>Solution Heat Treatment</th>
<th>Ageing</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>As received</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>910F, 1h</td>
<td>4 days at room temperature 24h at 250F</td>
</tr>
<tr>
<td>C</td>
<td>950F, 2h</td>
<td>4 days at room temperature 24h at 250F</td>
</tr>
<tr>
<td>MA-87</td>
<td>910F, 2h plus stretched</td>
<td>24h at 250F, 4h at 325F</td>
</tr>
</tbody>
</table>
Paciej and Agarwala (1988) worked on the effects of fabrication and processing on the corrosion susceptibility of metal matrix composite. In their previous works, they found that the techniques used for fabricating and processing a MMC adversely affected the MMC corrosion susceptibility. Corrosion and electrochemical investigations were conducted on a PM SiC<sub>p</sub>/AA 7091Al-T6 MMC in 3.5% NaCl. The factors were listed as follows: (1) elemental segregation, (2) voids, (3) poor homogeneity of reinforcement phase, (4) unstringered PM Al alloy material, (5) recrystallization of MMC portions and nonuniform plastic deformation caused by billet extrusion, and (6) residual stresses and cold worked regions not removed by the conventional solution heat treatment.

<table>
<thead>
<tr>
<th>Electrochemical Parameters</th>
<th>Al/SiC&lt;sub&gt;p&lt;/sub&gt;-MMC Temper</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>MA-87</th>
</tr>
</thead>
<tbody>
<tr>
<td>E&lt;sub&gt;a&lt;/sub&gt; mV</td>
<td>-831</td>
<td>-724</td>
<td>-724</td>
<td>-738</td>
<td></td>
</tr>
<tr>
<td>R&lt;sub&gt;p&lt;/sub&gt; Ω·cm&lt;sup&gt;2&lt;/sup&gt;</td>
<td>2.62</td>
<td>12.8</td>
<td>22.8</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>E(i=0) mV</td>
<td>-840</td>
<td>-798</td>
<td>-798</td>
<td>-810</td>
<td></td>
</tr>
<tr>
<td>i&lt;sub&gt;corr&lt;/sub&gt; A/cm&lt;sup&gt;2&lt;/sup&gt;</td>
<td>630</td>
<td>250</td>
<td>200</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

The materials used for recent study were Alcoa MM-87 alloy and a 20 vol% SiC<sub>p</sub>-PM AA7091 Al MMC. To produce the plate material the extrusion ratio was changed from 12 to 1 (used before) to 20 to 1 to enhance MMC homogeneity and to decrease matrix porosity and the size of inclusions. Heat treatment times and temperatures used, for all specimens, are listed in Table 2.8. Immersion tests and electrochemical measurements in both pH 2 and 6 solutions showed that the corrosion rates of MMC and the pH value increased rapidly in the first 3 days, and
then a decrease in corrosion rate was observed for all specimens as the exposure time was increased to 15 days, with only a slight increase in solution pH for each solution. Typical electrochemical parameters are listed in Table 2.9 and Table 2.10. The authors found that SiC\textsubscript{p} reinforced MMC did not exhibit any abnormal corrosion behaviour, as had been observed in their previous work on the SiC\textsubscript{w}/Al MMC, but clustered areas of SiC particles were regions of enhanced corrosion attack. The MMC corrosion resistance was improved by a combined effect of a modified solution heat treatment and a high extrusion ratio. Solution heat treatment of the as-received materials caused an increase in the void content of the MMC which could be responsible for the decrease in corrosion resistance. Expansion and contraction of the SiC particles resulted in a high dislocation density near SiC\textsubscript{p} -matrix interface during heating and water quenching, and consequently an increase in the amount of active phase precipitating during subsequent ageing.

Table 2.10 Typical Electrochemical Parameters of Materials in 3.5% NaCl Solutions (Paciej and Agarwala, 1988).

<table>
<thead>
<tr>
<th>Electrochemical Parameters</th>
<th>Al/SiC\textsubscript{p}-MMC Temper</th>
<th>MA-87</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>E\textsubscript{m} mV</td>
<td>-835</td>
<td>-845</td>
</tr>
<tr>
<td>R\textsubscript{p}(1) \Omega \text{cm}^2</td>
<td>6.61E+3</td>
<td>7.53E+3</td>
</tr>
<tr>
<td>E(i=0) mV</td>
<td>-926</td>
<td>-888</td>
</tr>
<tr>
<td>R\textsubscript{p}(2) \Omega \text{cm}^2</td>
<td>34.9E+3</td>
<td>35.1E+3</td>
</tr>
<tr>
<td>i\textsubscript{corr} A/cm\textsuperscript{2}</td>
<td>9.0E-7</td>
<td>4.0E-7</td>
</tr>
</tbody>
</table>

(1) Value measured after $E\textsubscript{m}$ reached steady state.

(2) Calculated from potentiodynamic polarization plot.
Corrosion Protection
Mansfeld et al (1986, 1987, 1988, 1989, and 1990) were interested in corrosion protection of metal matrix composites. For a Al/PM64 10% SiC composite, sulphuric acid-anodized and hot water sealed, they concluded that this kind of anodization treatment was not as effective as it was for the corresponding wrought alloys. The properties of the anodized layer must be quite different from those produced with same treatment. The presence of SiC particles on the surface produced these changes. In their further work, they observed an increase of the corrosion resistance after the passivation in 1000 ppm CeCl$_3$. However the corrosion resistance of the passivated Al/SiC tended to decrease with time. After three months immersion in NaCl, crevice corrosion was detected for Al/SiC. Since crevice corrosion did not occur for any of the other Al alloys and Al-based MMCs, they concluded that it was the result of the presence of the SiC particulates.

2.3.2 Other Metal Matrix Composites

B/Al MMCs
Some literature (Evans and Braddick 1971, Sedriks et al 1971, Pohlmian 1978) indicated that B/Al MMCs suffered severe attack at the B/Al matrix interface in Cl-$^-$containing solution. A study had been made of the corrosion behaviour of diffusion bonded 2024 Al alloy-unidirectional boron filament composites in aqueous chloride solution by Sedriks et al. They attributed the preferential attack to the presence of an "anodic site" at the interfaces, possibly due to imperfect bonding and the pre-existence of fissures yielding crevice corrosion. Pohlmian examined B/2024 Al and B/6061 Al composites prepared by hot pressing with immersion, alternate immersion, or spray tests in NaCl solutions. An explanation for the preferential attack of the metal/fibre interfacial area was given. Preferential attack was not caused solely by increasing the number of anodic sites due to the creation of additional voids causing an attack of the intermetallic, but was also caused by
galvanic corrosion between the intermetallic and the aluminium matrix causing preferential attack of the aluminium. Kiselev et al (1987) found that the corrosion resistance of AD1-25% B fibre MMC was lower than the AD1 Al alloy when the potentials were more negative than the potential for pitting formation. They attributed this to the defective condition of passivating films on the MMC resulting from internal stresses.

**Al₂O₃/Al MMCs**

So far, no evidence of galvanic corrosion between alumina Al₂O₃ and Al has been reported. Champion et al (1978) exposed DuPont FP Al₂O₃/Al-2% Li alloy for up to 90 days to eight accelerated corrosion tests solutions commonly used for testing wrought aluminium alloys. No evidence of severe attack at the interface was detected. Weight losses in most cases were only modestly higher than those of 6061 Al-T6. Comparisons made with 2219 Al-T87 alloy in a few cases showed the composite to be superior. Yang and Metzger (1981) examined Al₂O₃/Al-2% Mg in an NaCl-H₂O₂ accelerated test plus polarization studies. Severe selective attack in the matrix adjacent to the fibres was found. This was attributed to active dissolution of a Mg₅Al₈ phase located near the fibre. Otani et al (1989) studied Al₂O₃/Al, Al₂O₃/357 Al. It was found that attack was concentrated on the eutectic phase. They attributed it to FeAl₆ and Al-Si eutectic.

**Graphite (Gr)/Al MMCs**

These composites are prepared typically by coating the fibres with, for example, TiB₂, infiltration of fibre bundles with liquid aluminium to form composites wires, and hot pressing of these wires into plate. Because graphite provides a good cathode and has a free corrosion potential some 1 V higher than that of aluminium, there was concern from the start about galvanic coupling effects in these composites. Metzger, Fishman and Turnbull summarized several researchers investigation. Three distinct corrosion problems emerged: (1) galvanic corrosion (2) hydrolysis of the Al₄C₃ formed during processing and (3) preferential corrosion
of diffusion bonded regions at foil-foil, fibre-foil and fibre-fibre interfaces. Since the outermost skin of the composite is the aluminium alloy foil, corrosion is considered to be proceeded by penetration of the foil by pitting followed by more general corrosion in the form of exfoliation, swelling and eventually disintegration of the composites due to the wedging action of corrosion product formed in crevices.

Aylor and Moran (1985) conducted tests on Gr/6061 Al. Electrochemical tests results indicated that the accelerated Gr/Al corrosion was not predominantly due to classical galvanic corrosion. They suggested that carbon diffused into the aluminium at the reinforcement-matrix interfaces during fabrication, which caused a decrease in the surface film integrity at these localities and rendered the composite more susceptible to breakdown.

Dash (1989) investigated the mechanism of corrosion control of Gr/Al by using salt fog and immersion exposures, anodic and cathodic electrochemical polarizations, and galvanic coupling experiments of the MMCs and their constituents. The corrosion mechanism was divided into three steps. Stage I, the penetration of the corrosive environment into the interior of the MMC caused by (a) pitting of the fail, (b) mechanical or processing surface defect, or (c) capillary wicking of the solution down exposed fibres. Stage II, galvanic corrosion of the Al at the Gr/Al interface driven by the reduction of O on the graphite fibres. Stage III, corrosion/mechanical rupture of the MMC caused by wedging of the hydrated corrosion products in the confined spaces of the MMC.

Dutta et al (1991) investigated the corrosion behaviour of 0/90 cross-plied P130x graphite fibre reinforced 6063 Al composite laminates in deaerated and aerated aqueous Na$_2$SO$_4$ and NaCl solutions. It was found that galvanic corrosion was the dominant factor in both solutions. Even when graphite was not exposed to solutions, pitting of the surface foil was followed by galvanic attack of the matrix once the pit penetrated to the underlying graphite fibres.
Hihara and Latanision (1991) found that G/Al MMCs were susceptible to localized corrosion in Cl-free Na\textsubscript{2}SO\textsubscript{4} solution in which Al (e.g. 6061-T6) should be passive. The pitting was found to be caused by residual microstructure chloride originating from the Ti-B VD method. In another paper (1990) by these authors, the galvanic corrosion rates were determined using the zero-resistance ammeter technique and from potentiodynamic polarization diagrams of ultra-pure Al, 6061-T6 Al, graphite fibre, SiC, TiB\textsubscript{2}, and a commercial graphite fibre/6061-T6 Al MMC. They found galvanic corrosion rates of Al matrix composites were high in aerated Cl-containing solutions. Oxygen reduction was found to be the primary cathodic reaction. Aluminium corroded by pitting. The corrosion rate was controlled by the rate of O\textsubscript{2} reduction, which was significantly greater on P100 G than on SiC. Therefore, G/Al MMCs should corrode many times faster than SiC/Al MMCs. In the absence of dissolved O\textsubscript{2}, galvanic corrosion should be negligible even if Cl\textsuperscript{−} was present.

Efforts to suppress galvanic corrosion in graphite/aluminium metal-matrix composites are in progress. Dash (1988) found that of graphite fibre-Al galvanic couples could be reduced by coating the graphite fibres with SiO\textsubscript{2} to retard the oxygen reduction reaction. Hihara and Latanision (1988) attempted to use cathodic protection as a means to control galvanic corrosion in Al-matrix composites, and found cathodic protection is unsuitable because Al is susceptible to overprotection in which case corrosion rates increase rather than decrease due to alkalization of the cathodic surface. In their recent work (1993), two additional methods were investigated, one is called the electrical insulation method, the other is the cathodic inhibition method. For the first method, the insulator should have very high resistance. An insulator having a resistivity of about 10\textsuperscript{17} Ωm will be required to insulate a 1 m long fibre with a 0.1 μm thick insulation layer. This makes the method difficult to implement. Cathodic inhibitors can reduce galvanic-corrosion current densities by 10-100 times. Their conclusion is that the eventual goal is to develop modified graphite fibres that do not catalyze O\textsubscript{2} reduction so that Gr/Al MMCs with inherent resistance to galvanic corrosion can be fabricated.
2.4 THE OBJECT OF THIS INVESTIGATION

Metal matrix composite materials have been undergoing active development in the past ten years. The attention paid to the corrosion behaviour of this kind of material has gradually increased. Almost all investigators have realized that SiC reinforced aluminium MMCs undergo more serious corrosion relative to the unreinforced matrix and that this is especially associated with the pitting problems. As mentioned before, several explanation are proposed, but none of them gives very direct evidence.

This investigation will be related to the aqueous corrosion of silicon carbide reinforced aluminium alloy matrix composites. The object is trying to provide a better understanding to the corrosion phenomena of MMC materials, and evaluate the detrimental factors inducing pitting corrosion. In order to achieve the goal, a method is developed to distinguish the local galvanic corrosion cell, and furthermore to estimate local corrosion rate. Simultaneous SAM/EDX is adopted as the main tool to analyses and map out the local chemical changes on the material surface after corrosion. A variety of proven techniques such as SEM, AFM, and imaging XPS will also be used in the investigation. Electrochemical experiments, which are useful tools in corrosion studies, are used to get a better understanding of the corrosion mechanism of SiC reinforced Al MMCs.
Chapter 3 Basic Instrument

3.1 THE INTERACTION BETWEEN ELECTRON BEAM AND SPECIMEN

As an accelerated electron penetrates a specimen, a series of signals will be generated. These signals give very useful information for understanding the microstructure and composition of a specimen.

Figure 3.1 A summary of the effects which may be detected when a primary beam of high energy electrons hits a specimen (Goodhew and Humphreys, 1988). Where A is Auger electron; S is secondary electron; B is backscattered electron; D is the diffraction pattern.

As shown in Figure 3.1, there are several possibilities for an electron which enters a material. One of them is that the injected electrons pass straight through the material. This has negligible probability except when the specimen is extremely thin.
The most common occurrence for the incident electrons is elastic scattering. The significant point about this type of scattering is that the electron does not lose significant energy in the process and therefore is not slowed down, but it does change its direction. Elastic scattering is important since elastically scattered electrons are the main contributors to diffraction patterns.

![Diagram](image)

**Figure 3.2** Inelastic scattered volume and escape depth.

When an electron from the beam enters a material, the highest probability is that it will interact with one of the orbital electrons of an atom and transfer part of its energy to the orbital electrons. As a result of these interactions a vacant electron site might be left in one of shells of the atom which is then in an exited state. The incident electron loses part of its energy and slows down as well as being changed in direction. This type of electron interaction is known as inelastic scattering and continues until the electron is devoid of energy and stopped in the specimen. The exited atom will give off its excess energy in many different ways, these lead to the so-called secondary effects which can give us much information about the composition and nature of the specimen.

In a ‘solid’ specimen many inelastic scattering will occur until the electron is
stopped or leaves by the surface it entered. Although it is difficult to measure this shape experimentally, it can be estimated by simulating the electron trajectories for a given materials and set of operating conditions by Monte Carlo calculations. The volume within which 95% or so of the primary electrons are brought to rest is generally referred to as the interaction volume. The volume involved in the production of secondary electrons, backscattered electrons, and X-rays forms a tear drop shape within the specimen (Figure 3.2).

3.1.1 Secondary Electrons

Secondary electrons are used to describe those electrons which escape from the specimen with energies less than 50 eV. They could be emitted by the primary electrons beam or by backscattered electrons at the point where they leave the specimen and could also be primary electrons themselves which having lost most of their energy reach the surface with a few eV remaining. Those produced by the primary beam at point of entry are the more numerous. Therefore the detected electron signal originates mainly from a region which is little larger than the diameter of the incident beam. That is why scanning electron microscopy (SEM) can give high spatial resolution. A typical estimate for the escape depth of secondary electrons is 20 to 200 Å for metals and 50 to 500 Å for insulators.

Secondary electrons are mostly detected by an Everhart-Thornley detector. These electrons are attracted toward the detector by a positive voltage of between 200 and 400 volts, which is applied to a cage at the front end of the detector. Once within the cage, the electrons are accelerated to strike a scintillator which then emits light. The light is transmitted through a light pipe, and into a photomultiplier which converts the photons into electrons, which may then be amplified and used to modulate the intensity of the cathode ray tube which scans across the screen (Chapman 1986) in unison with the scan of the probe across the sample.
3.1.2 Backscattered Electron Emission

There is no accurate definition for backscattered electrons. Normally they are considered as incident beam electrons that have been re-emitted from the specimen through multiple scattering. They have also been defined as the electrons which leave the specimen with kinetic energies greater than 50 eV. These will include (1) elastically scattered primaries which leave the specimen with only a small loss of energy, (2) diffused electrons which leave the specimen with a greater loss of energy, and (3) Auger electrons. They are most likely to have energy near to incident beam energy. The emission of backscattered electrons from a specimen is related to atomic number of the material involved, the higher the atomic number, the higher the backscatter coefficient.

Two kinds of detectors are normally used for detecting backscattered electrons, one is the scintillator detector, the other is the solid-state detector. Scintillator detectors are designed to maximize the solid angle of collection. The disadvantage is that they are bulky and may affect the working distance of the microscope. The advantage is their rapid response time. The mechanism of solid-state detectors is that backscattered electrons from the specimen impinge on a semiconductor and produce many electron-hole pairs. If a voltage is applied to the semiconductor, a current flow is generated, and then can subsequently be amplified. The signal is used to produce an image on the display system. The disadvantage is its relatively slow response time (Goodhew and Humphreys, 1988).

3.1.3 X-ray Emission

When an atom is left in an exited state, the orbital vacancies may be filled by an outer orbital electron accompanied by simultaneous energy release. If the vacant electron state is an outer state, the energy to be given off may be in visible range, this effect is known as cathodoluminescence. When the vacant electron state is an inner state, the amount of energy is located in X-ray range. The energy of X-ray
is then the difference between the two orbital energy levels and this is characteristic of the particular atom species (Figure 3.3).

![Figure 3.3 An inner orbital electron is ejected by incident electron, an outer electron quickly fills the vacancy and a characteristic x-ray is simultaneously emitted.](image)

The sampling volume for X-rays is almost as large as the interaction volume since X-rays generated deeply in a specimen can escape and be detected. The volume depends on the incident electron energy and the atomic number of the specimen. The shape of the exited volume depends on the angle of incidence of the electron beam.

There are two different methods to obtain X-ray data, one is the wavelength dispersive spectrometer (WDS), another is the energy dispersive spectrometer (EDS). The relation between wavelength and its energy is presented by the following equation:

$$E = \frac{hc}{\lambda}$$
where $E$ is the energy, $\lambda$ is the wavelength, $h$ is the Planck constant and $c$ is the speed of light.

EDS uses a solid-state X-ray detector which normally consists of piece of semiconducting silicon. Each incoming X-ray excites a number of electrons into conduction band of the silicon leaving an identical number of positively charged holes in the outer electron shells. If a voltage is applied across the semiconductor, a current will flow as each X-ray is absorbed in the detector and the magnitude of the current will be exactly proportional to the number of hole/electron pairs and hence the energy of the X-ray. Thin layers of gold are used on both surfaces of the detector so that the bias potential can be applied. A thin window of beryllium is necessary to prevent contamination of the detector by material from the sample. Unfortunately a Be window can absorb low energy X-rays, and only the elements heavier than sodium can be detected. Windowless detectors, or detectors with some special windows are now available, and these extend the analytical range down to boron. The basis of WDS is that the X-ray radiation coming from the specimen is diffracted by crystal spectrometer according to its wave length, so that X-rays of chosen wavelength are separated into characteristic Bragg angles. Rotation of the crystal allows each, in turn, to fall on a detector. The detector for WDS is a gas proportional counter. As each X-ray photon enters through a thin window, it transfer its energy to a photoelectron, which then ionizes the gas to give many ion-electron pairs. Comparing WDS and EDS, the following differences are identified:

a) WDS has higher energy resolution and peak-to-background ratio than EDS.
b) WDS has ability to detect X-rays from light elements which is impossible for EDS with a standard detector.
c) For EDS, X-rays of all detectable energies are collected at the same time, so a complete spectrum can be acquired in a few minutes.
d) The detector for EDS can be placed very close to the specimen and therefore collect the X-rays very efficiently.
Chapter 3 Basic Instrument

3.2 AUGER ELECTRON SPECTROSCOPY

As mentioned in last section, when an incident electron beam interacts with a
specimen, a series of secondary electrons will be irradiated from the specimen. The energy distribution of the ejected electrons looks typically like the presentation in Figure 3.5. At the primary beam energy there is a sharp peak in the spectrum due to electrons that have been elastically scattered back out of the specimen. At slightly lower energies there are smaller peaks due to electrons that have suffered characteristic losses, for instance through the excitation of a plasmon. At the other end of the spectrum is the large peak of 'true' secondary electrons. Between the elastic and the true secondary electron peak, some of the small peaks are due mostly to Auger emission.

![CountSi (x10^6)](image)

**Figure 3.5** A spectrum showing the secondary, Auger, plasmon and backscattered electrons.

The Auger effect was first found by French scientist, Pierre Auger, during the period 1923-6, when he was investigating both secondary- and tertiary-electron emission with cloud chamber (Auger, 1975). From his cloud chamber pictures he concluded that some kind of internal conversion changes potential energy into mechanical energy instead of producing an electromagnetic quantum following the
departure of the first electron.

Figure 3.6 The Auger process in O₂⁻. A K-shell electron is ejected by an incident electron, and then an outer electron from L₁ shell fills the vacancy in the K shell. The energy difference \( \Delta E \) is transferred to another electron in the L shell. If the energy is sufficient to overcome the work function \( \varphi \), this electron can escape from the atom via Auger transition. (After Ferguson, 1989)

3.2.1 Auger Process

An incoming electron with sufficient energy can remove a core electron from an atom and the resultant vacancy is filled by an electron from one of the outer shells. The exited state atom then will relax back towards the ground state by two possible paths. One of these paths is the radiative transition which was mentioned in the section of X-ray emission. Another important path is the non-radiative transition. The excess energy is transmitted to another of the electrons in the atom, which then has sufficient energy to leave the atom and the material. Its kinetic energy is then uniquely determined by the energy difference. This electron is known as an Auger
electron. The schematic process is displayed in Figure 3.6.

Considering the Auger process, a KL$_1$L$_{2,3}$ Auger transition of a free atom with atomic number $Z$ can be described as

$$E_{KL_{1}L_{2,3}}(Z) = E_{K}(Z) - E_{L_1}(Z) - E_{L_{2,3}}(Z+1)$$  \hspace{1cm} \text{Eq 3.2}$$

Where value $E(Z+1)$ indicates the use of the binding energy of the next element in the periodic table to approximate for the relaxation of levels following the core ionisation.

In the case of a solid, this should be rewritten as

$$E_{KL_{1}L_{2,3}}(Z) = E_{K}(Z) - E_{L_1}(Z) - E_{L_{2,3}}(Z+1) - \phi$$  \hspace{1cm} \text{Eq 3.3}$$

$\phi$ is the work function of material, it corresponds to the difference between the vacuum level and the specimen's Fermi Level. Experimentally, the measured value of kinetic energy of Auger electrons must contain the term $\phi_A$, which represents the work function of the analyser directly involved in the energy analysis.

The physically correct expression for the Auger energy is presented by

$$E_{ABC} = E_A - E_B - E_C - \mathcal{F}(BC;x) + R_x^{\text{in}} + R_x^{\text{ex}}$$  \hspace{1cm} \text{Eq 3.4}$$

Where $\mathcal{F}(BC;x)$ is the energy of interaction between the holes in B and C in the final state x and the $R_x$ are relaxation energies. $R_x^{\text{in}}$ is the intra-atomic relaxation energy, i.e. the relaxation energy appropriate to an isolated atom. $R_x^{\text{ex}}$ is extra-atomic relaxation energy, that is due to additional screening electrons are available from other atoms or from the valence band respectively (Briggs and Rivière, 1990).
The history of electron exited Auger electron spectroscopy was different from many related analytical techniques. Since characteristic Auger peaks are superimposed on a relatively high continuum of background which is caused by backscattered and secondary electrons and are very weak, the spectrum was always displayed in the differential mode to remove the background contribution. However, as the technique of AES has developed attention has moved back toward the direct spectrum as used in the present study. There are many practical reasons for this (Bishop, 1984):

1. Some elements show large chemical shifts which complicate quantitative measures in the differential mode, but the overall peak is not changed by the chemical state of the element involved.
2. In Auger mapping it is much easier in the direct spectrum to correct for the effect of specimen topography (Janssen et al, 1977).
3. When the noise in the direct specimen is comparable to the peak height many of the practice advantages of differentiation disappear as the overall visibility of the peak is better in the direct mode.
4. At the low beam currents necessary to achieve high spatial resolution the signal from the electron spectrometer drops to a level where direct counting can be used. In this condition the direct mode becomes experimentally the easiest approach to adopt.

There are several factors determining the Auger signal intensity \( I(XYZ) \) corresponding to the XYZ Auger transition.

\[
I = (4\pi)^{-1} \int_0^\infty \int_0^{\pi} N(I_p \sec \phi K) (\sigma_p \exp(-z \sec \phi/\lambda) (1+r)) \, dz \, d\omega \quad \text{Eq 3.5}
\]

Where the symbols have the following meanings.

\( \omega \) the solid angle subtended by the analyser at the sample.
N the concentration of the species giving the peak.

$I_p$ the primary beam current.

$\phi$ the angle of incidence of primary beam.

$\sigma$ the ionisation cross-section for the core hole.

$P$ the probability of Auger de-excitation of this core.

$\lambda$ the inelastic mean free path of the escaping electron.

$K$ the probability of inelastic escaping electron being collected by the analyser.

$z$ the depth at which the electron is generated below the surface.

$r$ the backscattering coefficient, determining the probability that the Auger electron is excited by backscattered primary, or energetic secondary electrons.

Until now no simple semi-empirical formula will produce a set of usable relative intensities for the calculation of Auger transition. Even the complex formulations that have to be used by the theoreticians, although successful in the accurate prediction of intensities in the free atom, are not applicable to the solid state.

The escape depth for Auger electrons is the distance that an Auger electron, once created, can travel before being inelastically scattered and no longer appearing in the Auger electron peak. It is normally called the inelastic mean free path, $\lambda$. Seah and Dench (1979) made a thorough survey of escape depths and provided a set of relations for different cases of material over the energy range 1 eV - 6 keV:

For elements:

$$\lambda = 538E^{-2} + 0.41(\alpha E)^{0.5} \text{ monolayers} \quad \text{Eq 3.6}$$

For inorganic compounds:

$$\lambda = 2170E^{-2} + 0.72(\alpha E)^{0.5} \text{ monolayer} \quad \text{Eq 3.7}$$

For organic compounds:

$$\lambda = 49E^{-2} + 0.11E^{0.5} \text{ mg/m}^2 \quad \text{Eq 3.8}$$

Where $E$ is the energy of the electron in eV, $\alpha$ is the monolayer thickness measured in nanometres.
3.2.2 Instrument

Although the Auger process was found in 1923, studies of the emission of Auger electrons from surfaces progressed slowly. In 1967, Harris using a 127° cylindrical deflector energy analyser, showed the advantage of determining the derivative of the energy distribution function. Later, MacDonald in 1969 succeeded in obtaining an Auger spectrum from a spot 5 µm in size by using a coaxial-cylinder electron spectrometer and his basic idea was extended. Now the equipment based upon all these approaches became available commercially.

The basic AES system is built around the electron gun and the electron energy analyser. The electron gun is the source of an incident electron beam which is used to ionize the core levels and so initiate the Auger process. In most cases the electron source is thermionic, such as a tungsten hairpin filament or a crystal of lanthanum hexaboride, but for the highest spatial resolution the brighter field emission source may be used. Either magnetic or electrostatic electron lenses are used to form the probe.

The heart of the AES technique is the measurement of an electron energy spectrum. Such an analysis is performed by an electron energy analyser which is often called a spectrometer. Analysers can be based upon either magnetic or electrostatic principles. Only electrostatic analysers have been applied to Auger analysis since magnetic analysers are not easy to construct and handle in an UHV environment. There are many different types of electrostatic analyser and several of them have been tried at different times by various workers, but the most commonly used analyser for AES is the cylindrical mirror analyser (CMA) because of its higher transmission. The concentric hemispherical analyser (CHA) tended to be used mainly in combined AES/XPS instruments. However, as the transmission of the modern CHA with an optimised input lens and multichannel detectors can approach or even exceed that of CMA, the CHA is being increasingly used for AES.
Chapter 3 Basic Instrument

An electron detector is normally fitted in AES instrument to record secondary electron images. This kind of detector was briefly mentioned in secondary electron section.

An ion gun is quite necessary for AES. An important use is in depth profiling and another use is for specimen cleaning. The three most widely employed types of ion source for surface science are the cold cathode static spot gun, the electron impact ion source, and the duoplasmatron type of ion gun (Watts, 1990).

A UHV environment is an essential requirement for almost every technique of surface analysis available today. Many of the constituent parts, such as electron energy analysers, electron and ion source, electron detectors, and X-ray will operate only under high vacuum or ultra-high vacuum conditions. It is now generally accepted that AES must be carried out in the pressure range of $10^{-8}$ to $10^{-10}$ mbar. UHV system can maintain the sample chamber and analyser at a pressure so that the electrons have a long mean free path relative to the internal dimensions of the spectrometer, and it also can reduce the partial pressure of reactive residual gases to a level that will not unduly contaminate the sample surface and interface with the study of that surface. UHV conditions are achieved through the use of stainless steel and glass construction materials combined with suitable UHV pumping facilities.

3.2.3 Auger Maps

It is important for the researchers to know the characterisation of the chemical composition of a particular area, and the Auger maps can meet the requirement. Initially imaging was found to be of limited use because maps took a long time to record and not only chemical information, but also topographical effects were included in them (Bishop 1989). As the computer has come into use, the latter problem has been largely overcome by normalising the peak intensity to the background. The image recording time is also much reduced on modern
instruments and low intensity maps can also benefit from smoothing or the application of non-linear intensity transforms to highlight poorly resolved features.

![Auger spectrum of aluminium oxide](image)

**Figure 3.7** An Auger spectrum of aluminium oxide. The primary beam-solid interaction results in a total electron signal which is composed of electrons created by different processes (Baker and Castle, 1994).

To remove the topographical effects, one background map is also required for each peak map. In practice, a channel from the background on the high kinetic energy side of the peak is acceptable as background (Baker and Castle 1994). The high KE side is used as the low kinetic energy side contains a contribution from inelastically scattered Auger electrons (Figure 3.7). So the low kinetic energy background intensity is not as good as the high kinetic energy background intensity in revealing the real background.

The data handling processes are extremely important for Auger maps due to the approximate corrections that are required for the following complicating factors: (i)
The background beneath each peak in the spectrum. (ii) The topographical contribution to the signal; arising since the incidence and take-off angles vary with incident beam position and the Auger yield will vary even if the concentration of the element being imaged does not vary. (iii) The fluctuation of incident current during the long acquisition time. Two simplest algorithms are used, either

\[
\frac{\text{Peak} - \text{Background}}{\text{background}} \quad \text{or} \quad \frac{\text{Peak} - \text{Background}}{\text{Peak} + \text{background}}
\]

The first one was proposed by Todd and Poppa (1978) and is in widespread use. Prutton et al considered the second one is a more effective corrector for surface topography.

There are two modes for data acquisition of analytical images, one is scanning mode, the other is direct mode (Prutton 1992). For direct imaging methods, a large area of sample is irradiated. The analyser is of a type which images the emitting region of the sample onto a detector array. Imaging XPS, which will be brought up later, uses direct imaging methods since X-rays are not as easy to focus as an electron beam. Scanning mode is used in scanning Auger microscopy. A finely focused electron beam is used to scan across the sample under study. The Auger electrons, created with defined kinetic energy, are collected by the analyser/detector and the signal measured is stored in the memory of a control computer. For Auger maps, there are several data acquisition pathways. One is sequential image acquisition, in which a series of energy channel maps is collected one after another. This takes relatively short time, but drift may exist both in mechanical arrangements for holding the sample in a fixed position with respect to the electron beam and in the voltages applied to the scanning electrodes which determine the position of the beam on the sample. If corresponding pixels in each image of a set do not correspond to the same place on the surface then quantitative analysis of the composition at that place becomes impossible. A solution to this problem is to try to collect Auger electrons with all energies simultaneously, this
seems impossible unless multi-analysers are used. A compromise that can be made is to collect all the electron energies required by switching the analyser energy rapidly at a given pixel. The same procedure is repeated for the other pixels, but this tends to have an unacceptable computing 'overhead' resulting from the sum of all the switching operations. Thus in this work, the energy is constant for a given line, the intensities are collected and stored and then the analyser changed to the next required energy until all have been collected line by line (Figure 3.8). This method takes relatively less time than switching the analyser energy for each pixel. The information in corresponding pixels of the images in a image set comes from very nearly the same place on the surface in this kind of quasi-parallel image acquisition.

**Figure 3.8** Schematic presentation of Auger scanning model. The scanning order is pixel, line, energy channel and next line.
3.3 MA500 AUGER LAB

The MA500 is a scanning Auger electron microscope manufactured by VG scientific limited, UK in the early 1980's (Figure 3.9). It was one of the first of new generation of high resolution surface analysis instruments at that time and was the first to be designed as a combined scanning Auger / X-ray microprobe system. Besides the scanning Auger microscope, some other facilities were equipped, for example X-ray photoelectron spectroscopy (XPS), electron dispersive X-ray analysis (EDX), low energy electron loss spectroscopy, and X-ray fluorescence spectroscopy (XRF). As the scanning argon ion gun was equipped and some new computer software was developed, the MA500 became a much more powerful instrument which is now used in very large area of studies.

Figure 3.9 VG MA500 -- Auger Electron Microscope.
Figure 3.5 The arrangement of MA500 instrument chamber.
3.3.1 General Description of MA500

The arrangement of the MA500 instrument chambers is shown in Figure 3.10. On the right is a fast entry lock. Since the volume of the fast entry lock is very small and dry nitrogen is used to let the system vacuum up, faster pump down to rough vacuum can be obtained. In this case the vacuum will not decrease a lot when a specimen is transferred from the fast entry lock to the preparation chamber. The preparation chamber is normally kept at ultra high vacuum by using a diffusion pump. Facilities, such as the ion etching gun and a specimen fracture stage are attached to the preparation chamber. The ion gun is used to clean the specimen which will be analysed. The fracture stage can fracture specimens in UHV so that the virgin surface can be analysed immediately. This is quite necessary for the investigation of the basic mechanisms of fracture. The main part of this instrument is the analyser chamber. The electron gun system, X-ray source, electron analyser, X-ray detector, secondary electron detector, and scanning ion gun are all fitted in this vessel (Figure 3.11).

Figure 3.11 Spatial distribution of sources and detectors in MA500.
3.3.2 The Electron Gun

The electron gun of MA500 is an electromagnetic gun which operates between 2-30 kV with a variable spot size which is better than 500 Å at a sample current of approximately $10^{-9}$ A. The filament can be a tungsten hairpin or sometimes LaB$_6$. There are two magnetic condenser lenses to reduce the beam diameter and a magnetic objective lens for focusing. The beam spot size, $d$, is related to the beam current, according to the experimentally derived relationship.

$$d = 66\sqrt{i}$$  \hspace{1cm} \text{Eq 3.11}$$

where $d$ is in nanometres and $i$ in nA. A magnetic deflection system and magnetic stigmator are mounted around the central tube inside the objective lens. Astigmatism is removed via the stigmator and finally two orthogonal sets of coils allow scanning of the beam. A sliding plate allows any one of three final apertures of different sizes or wide open to be selected. Figure 3.12 schematically illustrates
the position of the components of the electron gun.

![Diagram of concentric hemispherical analyser](image)

**Figure 3.13** The schematic arrangement of concentric hemispherical analyser.

### 3.3.3 The Electron Analyser

The electron energy analyser of the MA500 instrument is a $150^\circ$ concentric hemispherical analyser (CHA) with a mean radius of 10 cm. A CHA is sometimes called the spherical sector analyser or the spherical deflection analyser in the literature. The basic form of a CHA is shown diagrammatically in Figure 3.13. Two hemispheres of radii $R_1$ (inner) and $R_2$ (outer) are positioned concentrically. $R_0$ is the radius of the median equipotential surface. Potentials $V_1$ and $V_2$ are applied to the inner and outer spheres respectively with $V_2$ greater than $V_1$. If electrons of energy $E = eV_0$ (the pass energy) are injected tangentially to the
median surface at radius $R_0$, the transmission condition becomes

$$V_2 - V_1 = V_0 \left( \frac{R_2}{R_1} - \frac{R_1}{R_2} \right)$$

Eq 3.12

or

$$V_0 = H (V_2 - V_1) = H \Delta V$$

Eq 3.13

where

$$H = \frac{1}{\frac{R_2}{R_1} - \frac{R_1}{R_2}}$$

Eq 3.14

Where the voltage applied between outer and inner hemispheres will give the required resolution. The plate in front of the analyser hemispheres which contains the entry and exit slits is called the Herzog or 'H' plate. The retard voltage, $R$, which provides the required acceleration or deceleration to the electrons, emitted from the sample, is applied to this plate. The kinetic energy of the electron in the solid is then expressed in the following way:

$$KE = R + H\Delta V + \phi_A$$

Eq 3.15

where $H\Delta V$ is the pass energy, and $\phi_A$ is work function of the instrument. Three different size slits are available to control the angular dispersion of electrons passing through the analyser and hence its resolution. The size of the slits are 2, 1, and 0.5 mm. An electrostatic lens is fitted between the sample and the analyser to enable a large proportion of the electrons emitted by the sample to enter the analyser.

There are two operating models for the analyser, one is called constant analyser energy (CAE) modes, another is called constant retard ratio (CRR) mode. The constant analyser energy mode means that the analyser operates at a virtually constant pass energy, $\Delta E = \text{constant}$, so the resolution of the spectrum is constant across the entire energy range. For MA500 the pass energy can either be controlled manually or by computer. Under computer control, the choice for pass
energies are 2, 5, 10, 20, 50, 100, and 200 eV. Alternatively, the analyser can be operated in constant retardation mode and the potentials on the hemispheres varied so that the entire energy spectrum is swept through. This gives a constant resolving power, $\Delta E/E$. The retard ratio, $RR$, is defined by

$$RR = \frac{R + H\Delta V}{H\Delta V}$$  

Eq 3.16

This mode is operated particularly popular for AES as the analyser transmission is low at small values of the pass energy, thus effectively suppressing the high electron yield at the low energy side of the spectrum. The spectrometer control unit of MA500 allows a retard ratio of 1, 2, 4, 10, 20, 50, and 100:1 to be selected either manually or via computer control.

3.3.4 Other Facilities

A Si (Li) solid state X-ray detector system for EDX and XRF is installed in the MA500, supplied by Link system (UK). The principle of this kind of detector was mentioned in the X-ray section. The detector is mounted at 45° to the electron detector and at 60° to the electron beam. It has a 10 mm$^2$ active area and a sensitive depth of 3 mm. A 1 mm aperture is fitted in front of a beryllium window in order to reduce problems of detector saturation. The resolution is 158 eV FWHM for a peak at 5.9 keV.

The X-ray source for XPS is operated with the filament near earth potential and the anode at a positive potential of up to 15 kV. The twin anode source has magnesium on one side and aluminium on the other side. This gives the facility of two independent X-ray lines at 1253.6 and 1486.6 eV respectively.

A scanning ion gun model EX05 is mounted in the analyser chamber and operated through model 400 ion gun power supply. Ions are produced in an
electron impact source which generates a beam having a very low energy spread with precise control of beam flux. The ions are then accelerated to energies up to 5 keV and pass through an ion optical focusing and deflection system. This ion gun is used for depth profile or cleaning specimens.

3.3.5 Data System

The computer datasystem AN10000 series developed by Link system is used for collecting storing and processing Auger and EDX spectra and maps. It is also used to control parts of spectrometer functions, such as retarding potential, starting kinetic energy, range, number of scans, steps, dwell time, and the operation of an argon ion gun.

The AN10000 system divides the computer memory into two blocks, so it can acquire EDX and Auger spectra simultaneously. Both spectra are either obtained from point analysis or area analysis which are controlled by spectrometer. This can reduce the effect of spatial drift during the spectra acquisition which would occur if the EDX and Auger spectra were collected one after another from a point or a small area. The simultaneous acquisition obtains both the surface and the bulk information from exactly the same area of the specimen. Since the spectra range, steps, and number of scans can be controlled by computer, it allows spectra to be collected in their entirety, or it is possible to examine fine details of spectra.

The AN10000 software allows the acquisition of digital maps and linescans either in real-time or directly to the disk store, and allows previously acquired data to be displayed and processed in a variety of ways. Up to 18 digital images can be stored in the same experiment. These can either come from the Auger electron signal or the X-ray signal. A digital image is basically a 2-dimensional array of number which represent the intensities on a grid of picture elements or so-called 'pixels'. Different image resolutions can be selected, they are presented by 32x32, 64x64, 128x128, 512x512 pixels and 128X128 pixels are normally acceptable. The
maximum value for each pixel is 65535 when the first value is defined as 0, any values greater than this will be set to 65535. Since the image is in digital form, various mathematical operations can be applied on a pixel-by-pixel basis thus altering the data in the image.

Another powerful program in MA500 is called a scatter diagram (Yan, 1991). The Scatter diagram was first used in Auger image processing by Browning (1985). The schematic representation of a scatter diagram is shown in Figure 3.14. Suppose there are two images, map A and map B, obtained simultaneously. If the pixels which are located at the position of column x, row y (128x128 matrix) in each maps have intensity values A and B, then a scatter diagram is a plot in which points are marked on a field with coordinates (A,B). All equivalent pixel pairs plotted against each other will construct a scatter diagram. The number of clusters in the scatter diagram is equal to the number of different combinations of the signals in the image set. This means the number of clusters is related to the number of different kinds of regions (or phases) in the area of the surface. This diagram is therefore a useful tool for making an objective decision about how many phases in the
surface. Once having selected a cluster in the scatter diagram, a new rebuilt image can be constructed through the computer software giving a phase map of the surface. Thus, through scatter diagram and rebuilding programs two element maps are transformed to phase distribution maps.

### 3.4 XPS IMAGES

In X-ray photoelectron spectroscopy (XPS), the primary excitation is accomplished by irradiating the specimen by a source of more or less monochromatic X-rays. The X-rays cause photoionisation of atoms in the specimen and the response of the specimen (photoemission) is observed by measuring the energy spectrum of the emitted photoelectrons (Figure 3.15). The resultant photoelectrons have a binding energy \( E_b \) which is related to the X-ray energy \( h\nu \) and kinetic energy \( E_k \) by the Einstein relation

\[
E_b = h\nu - E_k - \varphi_{\text{specimen}} \tag{Eq 3.17}
\]

or

\[
E_b = h\nu - R - H\Delta V - \varphi_A \tag{Eq 3.18}
\]

Since the atomic structure of each element is distinct, measurement of the positions of one or more of the electron lines allows the ready identification of an element present at a sample surface. The sample depth in XPS, which is governed by the electron mean free path in the sample material, is essentially the same as AES.

XPS is also called ESCA which is the acronym of Electron Spectroscopy for Chemical Analysis. This title comes from the ability of this technique to present chemical states, which was first used by Siegbahn (1967). Another advantage of this technique is that the quantification of an XPS spectrum is quite straightforward and
more accurate than quantitative interpretation of Auger spectra. Due to the X-ray beam used to excite the photoelectron, XPS is relatively harmless to most materials, especially when compared with surface analysis techniques which depend upon ion (SIMS) or electron (AES) bombardment of the surface (Riggs & Parker, 1975).

Although XPS has its outstanding advantages as a kind of surface analysis technique, the lack of spatial resolution, normally the order of several millimetres, limits its applications in many areas. Within the last few years however, attempts have been made to improve spatial resolution both by focusing the incident X-rays and by imaging the emitted photoelectrons (Christie, 1989).

A new imaging photoelectron spectrometer - VG Scientific ESCASCOPE is now commercially available, which has a spatial resolution less than 10 µm (Coxon et al, 1990). The design of ESCASCOPE is similar to the standard ESCA instrument. Unlike the conventional instrument however, the transfer lens system has modified and operates in a different manner as shown in Figure 3.16. An extra image plane of lens (2) is placed between the objective lens (1), which is used to collect photoelectrons from the sample, and diffraction plane of lens (3). Another additional lens (5) is placed between analyser output plane and a 2-dimensional

Figure 3.15 The physical basis of XPS (Riggs & Parker, 1975).
position sensitive detector. Therefore electrons leaving a different point on the surface will enter the analyser at a different angle. Lens (5) can invert the transformation produced by lens (3) and recreates a real 2-dimensional energy filtered photoelectron image of the sample surface on 2-D position sensitive detector. This image is only dependent on the angle at which electrons pass through the analyser output plane. Recently, a new Fisons Instruments - ESCALAB 220i XL has appeared which has improved the spatial resolution to 1 μm. It is same as the VG Scientific ESCASCOPE, but an electromagnetic immersion lens is fitted below the sample. This improves the count rate and spatial resolution. Some XPS images in this work were collected on this instrument.
3.5 ELECTROCHEMICAL EXPERIMENT FACILITIES

The potentiostat is a useful tool in electrochemistry. The pioneering work was done by Hickling in 1942 for the automatic control of electrode potentials by electronic means. A modern electronic potentiostat is a significant improvement on the Hickling's first potentiostat.

![Diagram of a basic potentiostat](image)

**Figure 3.17** The basic potentiostat (Von Fraunhofer and Banks, 1972).

A potentiostat is essentially a three-terminal device, being used with an ancillary electrochemical cell and electrodes. The basic potentiostat incorporates a differential input inverting pre-amplifier (Figure 3.17) as the means of controlling the power amplifier from the potential difference or error signal $V_e$. It is in fact a closed loop system, operating with a large degree of negative feedback. The potentiostatic operation is obtained in the following way: When an error signal $V_e$ is produced in working electrode, it is amplified by the high gain voltage pre-amplifier, and the output signal is fed into the power amplifier. The direction of the output signal from the pre-amplifier is such that any increase of the error signal between the working electrode and reference electrode results in a reduced flow.
of current from the power amplifier. Consequently if a potential of the working electrode moves in a positive direction with respect to the reference electrode, the output current from the power amplifier is reduced, thereby minimising the error signal between the working and reference electrodes.

Model 173 Potentiostat/Galvanostat produced by EG&G Princeton Applied Research is employed in this project. The model 173 mainframe consists of two potential sources, some control circuits to switch the potential sources and determine their output level, and a high-power high speed Summing Amplifier. The instrument features a current capability of one ampere. A Model 178 Electrometer Probe is supplied with this instrument so that the potential at a high-impedance point (Reference Electrode) can be monitored. The Model 276 interface is a plug-in module for the Model 173 Potentiostat/Galvanostat that enables Model 173 to interact with an external computer for both experiment control and data acquisition. An Apple II computer acts as external computer, and computer software 332 is used in this study.

The cell normally contains three electrodes and an electrolyte of reasonably high conductivity. The three electrodes are: the 'working electrode' (W.E), the 'reference electrode' (R.E) and the 'auxiliary electrode' (A.E) which is also called 'counter electrode' (C.E). The working electrode is the specimen which will be investigated. The reference electrode should satisfy the following conditions: (1) reversibility of the electrode process; (2) sufficiently high exchange current density of the electrode process; (3) stability of the electrode material with respect to the electrolyte; (4) low temperature coefficient; (5) convenience in preparation, maintenance or use. A very versatile reference electrode is the saturated calomel electrode (S.C.E.), consisting of mercury, mercurous chloride and saturated potassium chloride solution, and it is used in this project. The auxiliary electrode should be made from a very stable materials which is difficult to be polarised. Platinum is the best material to act in this role and was used in this work.
Chapter 4 Micro-galvanic Corrosion Cell in SiC Reinforced Al MMCs and Al alloy

4.1 EXPERIMENTAL PROCEDURE

4.1.1 Materials

The materials used for this study were 6061 Al and 6061 Al reinforced with 15% SiC particles. They were fabricated by a powder metallurgy route and the size of SiC particles was less than 10 μm. Another material used here was 6061 Al reinforced with 47% unidirection continuous SiC fibre. The reinforcing SiC fibres belong to the SCS series and are about 140 μm in diameter. All materials mentioned above were supplied by BP and the details of manufacturing procedure and processing are confidential. The chemical composition of matrix alloy is listed in Table 4.1.

<table>
<thead>
<tr>
<th>Si</th>
<th>Cu</th>
<th>Mg</th>
<th>Cr</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>0.25</td>
<td>1.0</td>
<td>0.2</td>
<td>Rem</td>
</tr>
</tbody>
</table>

Specimens of Al alloy and SiC particle reinforced Al MMCs with an area about 7x8mm² were cut from plate of 2 mm in thickness to meet the requirements of Auger and EDX analysis. SiC/6061 Al specimens were cut perpendicularly to the axis of the fibres. All specimens were wet ground with grit using 320, 500, 1000 and
4000 SiC papers and followed by polishing with 3 μm and 1 μm diamond paste. OP-S was used for the final polishing to remove material both in mechanical and chemical ways. Specimens were ultrasonically cleaned in acetone and Milli-Q water, and then stored in a desiccator in order to grow an air-formed film.

Specific sites on the surface were identified for study and marked by a three-point box of indentations made using a Vickers micro-hardness tester. This enabled repeated observations of the same site in the scanning electron microscope. In this way, a specific area can be recognized by any of our electron optical instruments: it is essential for comparisons made before and after exposure to the test environment.

4.1.2 Corrosive Media

The test solutions, either 3% NaCl or various concentrations of MgCl$_2$·6H$_2$O, as specified in the text, were prepared from analytical grade NaCl or MgCl$_2$·6H$_2$O and Milli-Q water. The pH value was adjusted with 1 N NaOH or HCl to 3.8, 7.2 and 10.2 for 3% NaCl and to 7.0 for MgCl$_2$ solution.

Specimens were exposed to the test solution for 20 min and the surfaces to be investigated were kept upward. After exposure, specimens were moved into ultrapure water, immersed for a few seconds and then dried by blotting with tissue on a lower corner. The dry specimens were immediately transferred to the UHV system for further analysis.

A scanning electron microscope (SEM) was used to examine the same area of samples before and after corrosion. The corroded areas can be distinguished readily in such a comparison. SEM micrographs were acquired on a Cambridge S250 microscope at a beam potential of, normally, 20 kV. In order to find indentations more easily the specimens were tilted at 30°.
4.1.2 Surface Analysis

A high resolution scanning Auger spectrometer (VG MA500) was used for these studies. The main advantage of this instrument is that it gives, simultaneously, the Auger and Energy Dispersive X-ray (EDX) signals at the same point (Castle & Ke, 1990). These two modes give, respectively, information on the elemental distribution either from the surface (nm) or from the "bulk" (μm). This gives the perfect register between the pixels of the maps made in different modes which is essential for analysis by scatter diagrams.

![Figure 4.1.1](image-url) Two specially designed sample holders.

To limit the contamination and the increase of pressure in the analysis chamber, double-side adhesive tape and silver dag are avoided for use in AES analysis. Instead of that, two specially designed sample holders (Figure 4.1.1) were used, into which samples were clipped with small screws. An electron beam energy of 15 keV and a specimen current of 10 nA were employed. These conditions not only excite strong Auger electron and X-ray signals, but also give a satisfactory spatial resolution. The specimen was tilted at 60° for the maximum Auger signal and the spectrometer was operated at a constant retarding ratio of 4. A 50 ms dwell time
for each channel was used for Auger point analysis and the whole energy range was scanned five times. A single energy channel in peak and a single energy channel in background were selected for each element for Auger maps, and the signal from the whole peak energy range was collected for EDX maps (Figure 4.1.2). The dwell time was 100 ms for each pixel of Auger maps and 200 ms for EDX maps.
4.2 MICRO-GALVANIC CORROSION CELL IN SiC/6061 Al

SEM photographs (Figure 4.2.1) show the main features of the MMC. The SiC particles are recognisable because polishing causes them to stand proud of the surface since they are much harder than matrix alloy and there are also some voids in the materials, that, probably, can be attributed to the fabrication procedure. The backscattered image (Figure 4.2.1), however, enables some other particles to be distinguished from the SiC: these are composed of high atomic number elements because of their strong contrast against both the aluminium matrix and the SiC particles and are in fact various inclusions and intermetallic compounds.

4.2.1 Exposure to Neutral NaCl Solution

SEM photographs of SiCp/Al 6061 before and after exposure in 3% NaCl solution at pH value of 7.2 for 20 min (Figure 4.2.2) reveal no obvious changes around SiC particulates as a result of immersion. Certain particles, spasmodically scattered across the images, are surrounded by a darkened region. EDX spectra (Figure 4.2.3) of such particles show that two types of compositions can be identified: one type is mainly of Fe, Al, Si and a little Cu, whilst the other is a
compound of Ti. Neither Fe nor Ti is added as alloying elements in 6061 Al alloy as shown in Table 4.1, they are impurity elements introduced during fabrication.
Polmer (1981) and Van Lanker (1967) have described the processing procedure of commercial Al. About 40% iron, silica and titania are contained in bauxite from which aluminium is obtained. Production of aluminium from bauxite involves two
distinct processes. First, pure alumina (Al₂O₃) is extracted from bauxite. Secondly,
aluminium is reduced from alumina by carbon at high temperature. The extraction process involves digesting crushed bauxite with strong caustic soda solution at temperatures up to 240 °C. Alumina is extracted leaving an insoluble residue consisting largely of iron oxide and silica which is removed by filtration. The impurities of Fe, Si and Ti in aluminium matrix may be introduced in this process.

Table 4.2 Auger and EDX windows which were set for mapping.

<table>
<thead>
<tr>
<th>Element</th>
<th>Auger Peak (eV)</th>
<th>Auger Background (eV)</th>
<th>EDX Energy range (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>270</td>
<td>288</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>418</td>
<td>430</td>
<td>4.382-4.606</td>
</tr>
<tr>
<td>Cl</td>
<td>181</td>
<td>195</td>
<td>2.528-2.709</td>
</tr>
<tr>
<td>O</td>
<td>509</td>
<td>527</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>701</td>
<td>715</td>
<td>6.228-6.470</td>
</tr>
<tr>
<td>Cu</td>
<td>919</td>
<td>931</td>
<td>7.865-8.108</td>
</tr>
<tr>
<td>Mg</td>
<td>1175</td>
<td>1185</td>
<td>1.212-1.314</td>
</tr>
<tr>
<td>Al</td>
<td>1390</td>
<td>1407</td>
<td>1.517-1.639</td>
</tr>
<tr>
<td>Si</td>
<td>1617</td>
<td>1627</td>
<td>1.781-1.923</td>
</tr>
</tbody>
</table>

Figure 4.2.4 presents EDX and Auger maps made using energy windows (as shown in Table 4.2) set for the different elements using spectra acquired at representative points on the surface. The Auger maps are clustered on the top of the figure and
Figure 4.2.4 Auger/EDX maps of Fe containing intermetallic after 20 min exposure in 3% NaCl solution, pH=7.2.

EDX maps on the bottom: a secondary electron image is given at the bottom right-hand corner. The presence of an intermetallic compound, composed of Fe, Al and a small amount of Cu, is revealed most strongly in the EDX map for iron. The
Figure 4.2.5 Auger/EDX maps of Ti containing intermetallic after 20 min exposure in 3% NaCl solution, pH=7.2.

Auger maps show no significant signal for iron in the vicinity of the inclusion, indicating that the inclusion is fully covered by a deposit. The Auger and EDX maps for aluminium are superficially similar to that of oxygen (Auger mode only).
because of the dominating influence of the oxide film formed on the metal matrix. Comparison of the oxygen and aluminium maps shows, however, that the oxygen signal is stronger in a halo around the iron-containing inclusion. The Auger map of carbon is similar to the EDX and Auger maps for silicon, bright areas corresponding to the location of silicon carbide particles. Carbon is also found on the oxidized matrix surface. This is because of the contamination which is produced in the electrochemical exposure, in the air transfer, and also in ultra-high vacuum. However, it is noticeable that the carbon signal on the top surface of the intermetallic compound is lower than general on the surface. This is a phenomenon which we have observed to occur when a deposit of high surface area is formed during corrosion.

Figure 4.2.5 shows a region of the matrix containing a titanium-rich inclusion after exposure in neutral 3% NaCl solution. The location of the inclusion is identified by the EDX map for titanium. Titanium is also seen in the Auger maps, alone with nitrogen, suggesting the presence of titanium nitride in the inclusion. The clarity of the titanium Auger signal shows that these inclusions are not covered by a deposit to the same extent as the iron inclusions. However, as shown in the previous maps, the oxygen signal is at a maximum in the region around the inclusion, and carbon at a minimum on the top of inclusion.

### 4.2.2 PH Value of 3.8 and 10.2

The MMC has also been observed after exposure to sodium chloride solutions at a pH value of 3.8 and 10.2, with broadly similar findings to those reported above. Figure 4.2.6 gives the Auger and EDX maps which were obtained from a specimen exposed at a pH value of 10.2. The intermetallic compound in this field of view is composed of Fe, Al and some Cu, similar to those examined on the sample exposed at pH 7. The interesting thing here is the strength of the copper Auger signal relative to the X-ray signal, which is very weak. The reason for this is still not clear. One possibility is that the intermetallics, acting as cathodes, enable
deposition of copper on the surface. The source of the copper is unlikely to be the test solution, which was prepared from analytical grade reagents. The obvious source is the anodic reaction at the matrix alloy as 6061 Al contains a low concentration of copper.

Figure 4.2.6 Auger/EDX maps of Fe containing intermetallic after 20 min exposure in 3% NaCl solution, pH=10.2.
Figure 4.2.7 gives the Auger and EDX maps of a region of the specimen which was immersed at a pH value of 3.8. This surface carried a higher level of corrosion products than the samples exposed in neutral and alkaline solutions. In this series
of maps, there are two kinds of intermetallics, one is mainly composed of Ti and the other is Fe-containing. Both of these could be seen in the X-ray maps but neither could be seen in the Auger maps, illustrating the extent to which this surface is covered by corrosion products.

4.2.3 Scatter Diagram

Maps, such as those used here to illustrate the findings of the exposures to corrosive solutions, are highly subjective. The microscopist through the control which is exercised over colour and contrast brings to the attention of the reader the general or local concentrations of ions which are thought to be of interest. Some degree of objectivity can be introduced by seeking correlations of elements in fixed ratios, which point to the presence of particular phases or compounds. This is most readily done by using a scatter diagram.

Figure 4.2.8 Scatter diagram used for the maps in Figure 4.2.4. Top: scatter diagram and selected region, bottom: reconstructing maps.
The use of a scatter diagram is illustrated by means of the specimen which was corroded in neutral 3% NaCl solution, for which the raw data were given in the maps of Figure 4.2.4. The scatter diagrams are given on the top row of this figure and these show by coloured circles the pixels which have been selected as having significance in the maps reconstructed on the bottom row. In the middle pair, Figure 4.2.8b, we see the analysis based on the intensities of carbon and silicon Auger electrons in each of the 16,000 pixels. Two surface phases are set by identifying circular regions on the scatter diagram: one identifies the pixels which are high in both silicon and carbon, which correspond to SiC particles and are coloured green in the reconstructed map; the other region identifies the pixels which are low in silicon and carbon and this, plotted in blue, shows up the background which is mainly the matrix alloy. The scatter diagram in Figure 4.2.8a plots silicon against aluminium and illustrates the anti-correlation between these two elements. The reconstructed map of Figure 4.2.8b is reproduced here by plotting those pixels which are high in silicon but low in aluminium (green) and those pixels which are low in silicon but high in aluminium (blue).

The above figures illustrate some of the features of a scatter diagram analysis of data, viz: that the size of the clusters on the scatter diagram is related to the standard deviation in the analysis; that the relative intensities of the clusters is related to the number of pixels in each phase and thus to the relative areas of the phases on the map; that the line drawn through anti-correlation diagrams, such as that in 4.2.8a, intersects the axes with intercepts that correspond to the relative sensitivities of the two elements; and that the centre of the cluster, when corrected for the relative sensitivities, gives the mean composition of the phase.

In the right-hand side of the set of scatter diagrams, Figure 4.2.8c, a very strong correlation between aluminium and oxygen is seen. This clearly corresponds to the surface oxide phase covering the aluminium alloy of the matrix, this is readily confirmed by assigning a blue colour and showing that it matches the background in the other maps. Similarly the pixels (green) which contain neither aluminium nor oxygen match the outlines of the silicon carbide particles of the other maps.
Scatter diagrams can however be used, to examine the location of pixels which lie outside the major clusters. In this case, the pixels lying between the green and blue clusters have an intermediate intensity but the same ratio of aluminium to oxygen - they mainly pick out the phase boundary between silicon carbide and alumina. The low intensity probably corresponds to the prevailing spatial resolution of the Auger system which gives rise to low intensities as the signal falls in passing from one phase to the next. The examination of the pixels of lower intensities in aluminium and oxygen also shows up two particles, Figure 4.2.8c, which do not appear in the upper maps of silicon carbide. These are show the location of inclusions.

The strong oxygen signal might be a indication of electrochemical activity at the site of inclusions. This indication of electrochemical activity has been found at each of the pH levels studied in this work. In each case inclusions have been located and analyzed for the location of high oxygen pixels by use of a scatter diagram. The oxygen/aluminium ratio is given by the slope of a line passing through the origin on the Al/O diagram. Thus either all the pixels in a fan shaped region centred on such a line can be highlighted, or the circular cluster can be merely split into two halves with different Al/O ratios. Figure 4.2.9 shows an example of this approach used to show the presence of high oxygen/aluminium ratios in regions surrounding inclusions, which is marked with "x", at each pH. A similar analysis of a sample which has been exposed only to air shows no sign of enhanced oxygen at inclusions. The aluminium maps were obtained using the chemically shifted peak for the aluminium ion. Thus the oxygen/aluminium ratio does not reflect a change in oxide thickness but rather, a change in composition. It is not possible in the AES spectrum to distinguish between the hydroxide and the oxide ions but we must presume that an increase in oxygen content comes about as an increase in the hydroxyl component of a mixed aluminium oxyhydroxide. This would correspond to the deposition of corrosion product from the anodic activity induced by the cathodic inclusion.

The intensity of carbon signal is inversely proportional to that of the intensity of oxygen signal as shown in Figure 4.2.10. This is understandable, since the oxide
Figure 4.2.9 Different oxygen against aluminium ratio located at different place. a) before corrosion, b) exposed in 3% NaCl pH=7.2, c) exposed in 3% NaCl pH=10.2, d) exposed in 3% NaCl pH=3.8.

film only exists on the matrix surface and not on SiC particles surface where the carbon intensities are strong. However, an interesting thing is that a small cluster appears in the scatter diagram of carbon against oxygen at the place of low carbon
and middle oxygen intensity. When the pixels in this cluster are selected, it can be found from rebuilding the map, that most of them are located at the place where the intermetallic particle exists. This means that a low concentration of carbon exists on top of the surface of the intermetallic particle. This phenomenon can also be found after the specimens was exposed to NaCl solution at the pH values of 3.8 and 10.2 (Figure 4.2.11). On the contrary, the carbon signal at the site of an intermetallic particle has the same intensity as the matrix surface for the unexposed specimen. Considering the low concentration of carbon and the deposition of copper at the inclusion site as mentioned before, the inclusion site might act as cathode in the electrochemical activity during the corrosion process. In order to seek for the irrefutable evidence, the experiments given in the following paragraphs were designed.

Figure 4.2.10 The intensity of carbon against oxygen. The corroded specimens that were exposed to 3 % NaCl solution at pH value of 7.2 (top) and 10.2 (bottom) for 20 min.
4.2.4 Cathode Identification

Until now, the anodic area can be recognized through the existence of corrosion products which contain a high concentration of oxygen. The cathode area is still not clearly displayed in the maps, although the carbon signal is low on the top of intermetallic and, sometimes, deposition of copper can be found for the corroded specimen. In this case MgCl$_2$ solution as a corrosive environment is used to identify the cathode due to the change of pH value caused by cathodic reaction. The principle of reaction mechanism is shown in Figure 4.2.12. The anodic reaction is the oxidation of aluminium metal to aluminium ions. On the contrary, the cathodic reaction in neutral solution can reduce dissolved O$_2$. At the place where the cathodic reaction proceeds, the hydroxyl ion produced locally will likely absorb cations. When the square of concentration of hydroxide ion, produced by reduction
### Equation

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- = 4\text{OH}^- \]

### Diagram

**Figure 4.2.12** The increasing pH value in local area due to cathodic reaction makes Mg\(^{2+}\) in the solution deposit as Mg(OH)\(_2\) when the concentrations get to the solubility product.

of oxygen, times the concentration of magnesium is larger than the solubility product of magnesium hydroxide, then, magnesium hydroxide will deposit. This is easy to recognize by Auger maps since the magnesium and oxygen signals will be higher at this region.

Figure 4.2.13 displays the Auger and EDX maps of the sample after exposure in MgCl\(_2\) solution. A cluster with high intensity of magnesium and oxygen can be found in Auger maps, and it seems just on the top of intermetallics as compared with X-ray maps. Again, a scatter diagram is a useful tool for finding out the relationship between the intermetallic particle and the deposition of magnesium...
hydroxide. Figure 4.2.14a is the scatter diagram of Auger Mg against X-ray Fe, the
direct ratio means that the cluster with high concentration of Mg corresponds to the
particle of intermetallic. Due to diffusion of the hydroxyl ions, the concentration of
Mg decreases with the distance away from intermetallic particle.

Figure 4.2.13 Auger/EDX maps after 20 min exposure in 5.2% MgCl₂ solution pH=7.0.
The chlorine ions are concentrated in the anodic areas which can be found either from Auger map or X-ray map. The high intensity Cl\(^-\) in X-ray map concentrated in the deep place where holes appeared in second electron image, and high intensity Cl\(^-\) in Auger map located on more flat place near intermetallics. No Cl\(^-\) appeared in the cathodic area. Another phenomenon is that the Mg and O signals on the top of SiC particles are not higher than matrix, this means that the SiC particles do not act as cathodes in this situation.
From above results we realise that the intermetallic particle can form a micro-galvanic corrosion cell, the intermetallic particle plays the role of the cathode and the surrounding area the anode, thus causing the dissolution of aluminium.

4.3 ESTIMATION OF CATHODIC CURRENT DENSITY

4.3.1 The Principle of Estimation

The common cathodic reactions are related with: 1) reduction of noble metal ions in the solution; 2) the liberation of hydrogen gas; and 3) the reduction of oxygen gas dissolved in the solution. The reaction equations are listed as follows:

\[ \text{M}^{n+} + n\text{e}^- \rightarrow \text{M} \quad \text{Eq 4.2} \]

\[ 2\text{H}_2\text{O}^+ + 2\text{e} \rightarrow \text{H}_2 \uparrow + 2\text{H}_2\text{O} \quad \text{Eq 4.3} \]

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e} \rightarrow 4\text{OH}^- \quad \text{Eq 4.4} \]

Since the solution used here contains either Na\(^+\) or Mg\(^{2+}\), both of them have very low electro-potential, it is impossible for them to be reduced in normal condition.

Both of the remaining cathode reactions create a change in local pH value and this can be searched for by the use of a cation which has a sparingly soluble hydroxide. The most likely cathode reaction at nearly neutral pH values is the reduction of oxygen. The generation of hydroxyl ions will: 1) cause the local pH to increases; 2) react with hydrogen ions; 3) escape by diffusion; 4) escape by migration; and 5)
escape by convection. Since there is no stirring during the period of exposure and the potential problem of stirring by evolution of hydrogen gas is eliminated at near neutral pH values, the convection item can be neglected. For the migration item, the solution is maintained at 0.25 M NaCl + MgCl₂ and thus need not be considered due to the existence of large amounts of electrolyte compared with the concentration of hydroxyl ions. Considering all the situations, the local pH will rise until the rate of generation of hydroxyl ions is equal to their escape by diffusion or by reaction with hydrogen ions. This equilibrium is reached rapidly (Castle and Tremaine, 1979) and the current density, \(i/A\), is then directly related to the flux, \(J\), of ions to and from the cathode, ie:

\[
i/A = F (J_{OH^-} - J_{H^+})
\]

Eq 4.5

the negative sign being used to compensate the flux of hydrogen ions towards the electrode.

Substitution for the flux, using Fick's first law, provides an expression in terms of the local concentration gradients \(\Delta[OH]\) and \(\Delta[H]\), and the diffusion distance, \(\delta\):

\[
i/A = \frac{F}{\delta} (D_{OH^-}\Delta[OH^-] - D_{H^+}\Delta[H^+])
\]

Eq 4.6

Then Eq 4.6 can be rewritten in the following way:

\[
i/A = \frac{F}{\delta} \left[D_{OH^-}[OH^-]_{surf} - [OH^-]_{bulk} + D_{H^+}[H^+]_{bulk} - [H^+]_{surf}\right]
\]

Eq 4.7

It follows from Eq 4.7 that the maximum concentration of hydroxyl ions in the system will be found at the cathode and that it is a function of the current density. Thus addition of increasing quantities of magnesium ions to the electrolyte will, at
a critical concentration, cause the precipitation of \( \text{Mg(OH)}_2 \) at the cathode, and this is readily detected by SAM. The delineation of cathodes by this method has been shown by Daud (1982).

The determination of the current density through the cathode at this critical concentration is possible by solution of the equation derived from Eq 4.7 using the solubility product of the relevant hydroxide and the ionic product of water:

\[
\frac{\text{i}_\text{o}}{\text{A}} = \frac{\text{F}}{\delta} \left\{ \text{D}_{\text{OH}^-} \left( \frac{\text{K}_s}{[\text{Mg}^{2+}]} \right)^{\frac{1}{2}} - \frac{\text{K}_w}{[\text{H}^+]} \right\} + \text{D}_{\text{H}^+} \left[ [\text{H}^+] - \text{K}_w \left( \frac{[\text{Mg}^{2+}]}{\text{K}_s} \right)^{\frac{1}{2}} \right] \right\} \text{ Eq 4.8}
\]

Figure 4.3.1 Curves calculated from Eq 4.7 showing the relation between the current density and the critical concentration of Mg ions required for precipitation of \( \text{Mg(OH)}_2 \).

Castle (1993) has shown that, for near neutral electrolytes, only the first term of
Eq 4.8 is important and that the current density is almost independent of the bulk pH value over a range from pH6 to pH8.

The curves provided in Figure 4.3.1 are chosen to cover a range in diffusion length ranging from 1 μm to 10 μm. They show how the critical current density for the first observation of magnesium at the cathode will vary with the concentration of magnesium and the diffusion distance. The diffusion coefficients of hydrogen and hydroxyl ions were taken as 0.93 and $0.52 \times 10^{-8} \text{m}^2\text{s}^{-1}$ respectively; the solubility product for magnesium hydroxide was taken as $1.8 \times 10^{-11}$, and the pH value for the curves shown in Figure 4.3.1 was taken to be 7.0. In order to determine the cathodic current density two unknown factors need to be measured, one is the critical concentration of $\text{Mg}^{2+}$ for precipitation, another is the diffusion distance, $\delta$.

![Auger spectra](image)

**Figure 4.3.2** Auger spectra for the specimen which is immersed in 0.1 M MgCl$_2$ for 15 min. Top: acquired at intermetallic position, bottom: acquired from matrix.
4.3.2 Critical Concentration

The analytical evidence cited above leads to the conclusion that the principal electrochemical activity is associated with the sites of inclusions or intermetallics. Accordingly a set of experiments was carried out to estimate the current density at the intermetallic using the equations (Eq 4.8) derived earlier. MgCl₂ solutions at concentrations of 0.1 M, 0.01 M and 0.001 M were employed to bracket the critical concentration which will cause precipitation of Mg(OH)₂ at cathodic area.

Figure 4.3.3 Auger spectra obtained from the intermetallic on specimens immersed in MgCl₂ solution. Top: 0.1 M MgCl₂ solution, middle: 0.01 M MgCl₂ solution, bottom: 0.001 M MgCl₂ solution.

Figure 4.3.2 shows the Auger spectra for the specimen which was immersed in 0.1M MgCl₂ solution for 15 min. The spectrum on the top was acquired at the position
of the intermetallic and the characteristic magnesium peak appears at 1180 eV. The bottom spectrum was acquired from the aluminium matrix, the absence of magnesium giving evidence that the Mg peak at the inclusion does not result from inefficient rinsing after exposure. Figure 4.3.3 shows the magnesium spectra obtained from the sites of intermetallics on specimens immersed in the MgCl₂ solutions. The strong Mg peak in the spectrum is much diminished at 0.01 M and totally disappears at 0.001 M. Thus the critical concentration of MgCl₂ for precipitation of Mg(OH)₂ at a cathodic area is in the range of 0.001 M to 0.01 M.

![Graph](image)

**Figure 4.3.4** High energy resolution of narrow Auger spectrum for aluminium (CRR = 10).

### 4.3.3 Diffusion Distance

The model represented by the equation above is simply Fickian diffusion over a planar geometry. With separated electrodes, as found in a potentiostatically controlled experiment the parameter, δ, may be set equal to the thickness of the diffusion boundary layers. In micro-cells the diffusion takes place between adjacent
or concentric sites lying fully within the diffusion boundary layer. The consequences of this can be seen in SAM maps of anode/cathode distribution obtained by Ke (1989). In these the annular cathode around the anode has a radius of about 2r, where r is the radius of the central anode.

![Schematic representation of diffusion distance for hydroxide ions.](image)

**Figure 4.3.5** Schematic representation of diffusion distance for hydroxide ions.

From the high energy resolution (CRR = 10) narrow Auger spectrum (Figure 4.3.4), two main peaks can be found for aluminium at the normal matrix position, one is aluminium metal peak at the kinetic energy of 1394 eV which expresses the deeper layer information, another is aluminum oxide peak, 1387 eV, which expresses the very top layer of the surface film. The metal peak becomes very low at the position next to the intermetallic particle: this is the result of hydroxyl ion diffusion, which covers the oxide film with corrosion products, or the high pH value, which makes the surface film become much more thick. So the distance between the intermetallic particle/matrix interface to the position that intensity of aluminium
metal signal increases back to normal is considered as diffusion distance. The schematic representation is shown in Figure 4.3.5. Based on this idea, a set of Auger and EDX maps was collected at the area including a Fe containing cathodic

Figure 4.3.6 Top: Auger/EDX maps of Fe containing intermetallic after 20 min exposure in 3% NaCl solution, pH=7.2. Bottom: superimposition of Auger aluminium metal map and EDX Fe map.
particle (Figure 4.3.6), aluminium oxide and aluminium metal maps were acquired individually. It seems that there is no aluminium metal signal around the intermetallic particle, but we can find aluminium oxide and oxygen at that area. The lower part of Figure 4.3.6 is the superimposition of the Auger aluminium metal map and the EDX iron map. The distance from the green point to the blue point is almost the same length as the intermetallic particle’s diameter. So the diffusion distance is considered to be equal to the diameter of cathodic particle diameter. This result is reached in unanimity with Ke (1989).

4.3.4 Cathodic Current Density

From the above result we know that the critical concentration of MgCl₂ is between 0.001 to 0.01 M. Suppose the concentration of 0.01 M is accepted as the critical concentration. Then, since diffusion distance δ may be taken as 3 μm (twice the radius of this cathodic particle), the approximate cathodic current density can be read from the curve in Figure 4.3.1. The value so obtained is 0.7 mA/cm².

4.3.5 The Volume of Dissolved Aluminium

The cathodic current density is estimated by using the above calculation. In order to obtain an independent check on the value, the loss of aluminium in the surrounding anode is calculated through the following concept. Through the cathodic current density we can get the total cathodic current related with each cathode particle. As general idea, the total cathodic current is equal to the total anodic current,

\[ i_a = i_c \]  \hspace{1cm} \text{Eq 4.9,}

and after using the Faraday’s law, the following equation is generated.
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Where $W$ and $V$ are the weight and volume of dissolving aluminium respectively, $i_a$ is anodic current which equal to the cathodic current, $t$ is corrosion time, $F$ is Faraday's constant which equal to 96500 c/Jmol, $M_{Al}$ is atomic weight of aluminium, and $d$ is the density of aluminium.

An independent check was performed by measuring the volume of dissolved aluminium at the anodic area. The preparation of the specimen was same as before. The polished sample is corroded in 3% NaCl solution for 15 min. Confocal Laser Scanning Microscopy (CLSM) was used at first, but the resolution was not high enough to measure the depth of corroded area and the refraction of the oxide film also affected the measurement. Atomic Force Microscopy (AFM), which proved to be a useful tool, was used instead in this study. The top picture of Figure 4.3.7 is the SEM photograph related with a cathodic particle and an anodic halo. The lower one is the AFM micrograph of the same area as the top one. The vertical and horizontal distances between the particle surface and the corroded hole or the normal surface are displayed in red and green colour respectively. The volume of dissolved aluminium can be calculated by the following equation.

\[
V = \frac{i_a t}{3 F} \cdot M_{Al} \cdot \frac{1}{d} \quad \text{Eq 4.11}
\]

The volumes dissolved for the sample which was corroded for 15 min. have been calculated by both methods and are listed in Table 4.3.
These two results differ by a factor of four meaning that the estimated result is reasonable. The smaller value for the measured volume is probably due to the
corrosion products not removed fully from the anodic area, and some spill over of corrosion products into the cathodic area.

<table>
<thead>
<tr>
<th>Table 4.3 Comparison of measurement and estimation results</th>
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<tr>
<td>estimated volume</td>
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<td>measured volume</td>
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4.3.6 Estimation of Cathodic Current Density by Using Spherical Diffusion Model

In our practical situation, the intermetallic particle is very small. The diffusion of corrosion products, such as hydroxyl ions, is more likely to take place in a spherical way than in a plane sheet way. An approximation must be made since the intermetallic particle surface is a circular surface, not a spherical surface. In the steady state, the quantity of diffusing substance, $Q_1$, which passes through the spherical wall in time $t$ is given by

$$Q_1 = 4\pi Dt \frac{r^2}{\delta - r} (C_2 - C_1)$$  \hspace{1cm} \text{Eq 4.13}

The rate of transfer of diffusing substance from the particle surface is equal to the quantity of diffused substance divided by the area of the diffusion layer and the time. In the standard spherical diffusion model, the particle surface should be a spherical surface and thus the area should be $4\pi r^2$. In the real situation, the particle surface is a circular surface and the area is only $\pi r^2$. If the circular area is used, the rate of transfer of diffusing substance on the particle surface can be written by

$$J = \frac{4D \frac{r^2}{\delta - r}}{\delta - r} (C_2 - C_1)$$  \hspace{1cm} \text{Eq 4.14}$$
Considering our situation, and by applying Ficks first law, the cathodic current density on the cathode particle surface can be written as following:

$$i/A = \frac{4F}{r^2} \frac{r \delta}{\delta r} \left[ D_{OH}^{-}\left([OH^{-}]_{surf} - [OH^{-}]_{bulk}\right) + D_{H^+}\left([H^+]_{bulk} - [H^+]_{surf}\right) \right]$$  \text{Eq 4.1}$$

$$i/A = \frac{4F}{r^2} \frac{r \delta}{\delta r} \left\{ D_{OH}^{-} \left[ \frac{1}{\left([Mg^{2+}]\right)^{1/2}} - \frac{K_w}{[H^+]} \right] + D_{H^+} \left[ [H^+] - K_w \left(\frac{[Mg^{2+}]}{K_s}\right)^{1/2}\right] \right\}$$  \text{Eq 4.2}$$

As the critical concentration of Mg$^{2+}$ for the deposition of Mg(OH)$_2$ has been evaluated, and supposing the diffusion distance of hydroxyl ion is equal to the diameter of cathodic particle, the estimated cathodic current density can be calculated by using Eq 4.2. In this case, the cathodic current density on intermetallic particle surface is 8.4 mA/cm$^2$.

It is understandable that diffusion of a substance is more efficient in three dimensions than in one dimension, so the cathodic current density calculated by using the spherical diffusion model is correspondingly greater than when the plane sheet diffusion model is used.

\textbf{4.4 THE EFFECT OF INTERMETALLIC PARTICLES IN 6061 Al ALLOY}

The previous results show that two intermetallic phases exist in 15 % SiC$_p$/6061 Al MMC, one contains Al, Fe, Si and a little Cu, another mainly contains Ti. The intermetallic particles play the main role in forming micro-galvanic corrosion cells
with the matrix. Therefore a comparison study was performed on the matrix alloy itself.

Figure 4.4.1 is the SEM micrograph of 6061 Al that was polished to 1 μm. Three big indentation marks are used to recognise the specific position before and after corrosion. From this picture we can find some white particles with different shapes and sizes, and some black spots that look like holes exist in the specimen as well. A careful, point, Auger and EDX analysis was performed on each of the interesting positions.

![Figure 4.4.1 SEM micrographs of polished 6061 Al.](image)

The EDX spectrum (Figure 4.4.2) shows that the big white particle contains Al, Si, Fe and a little Cu. The Auger spectrum shows that aluminium oxide and carbon contamination exists on the surface. This kind of particle can also be found in 15 % SiC₆/6061 Al MMC. Different compositions have been observed from some of the smaller white particles (Figure 4.4.3) that are mainly composed of Al and Si. As mentioned in chapter 2, there is no such phase existing in 6061 Al that only
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Figure 4.4.2 Auger and EDX spectra of the big white phase in 6061 Al alloy.

Figure 4.4.3 Auger and EDX spectra obtained from the small white particle in 6061 Al alloy.

contains Al and Si. In this case the aluminium signal may come from the surrounding aluminium matrix. The small white particle is probably a Si particle. SEM photograph shows some black spots, they look like holes in the aluminium.
Figure 4.4.4 Auger and EDX spectra obtained at the black spot.

Figure 4.4.5 Auger and EDX spectra obtained at the point of big white particle. The specimen has been exposed to 1 M MgCl$_2$ solution at pH value of 7 for 10 min.

Point analysis on the spot shows that Al and Si peaks appear in the EDX spectrum and C, O, Al and Si appear in the Auger spectrum (Figure 4.4.4). The peak position for silicon in the Auger spectrum is shifted to 1608 eV; it most likely
contains SiO$_2$, as the pure silicon KLL peak should be at 1619 eV.

![Figure 4.4.6 Auger and EDX spectra obtained at the point of Si containing particle. The specimen was exposed in 1 M MgCl$_2$ solution at pH value of 7 for 10 min.](image)

 Ion decoration was used for the 6061 Al specimen to identify the cathodic sites by immersing specimens in 1 M MgCl$_2$ solution at pH value of 7. Examination of Auger and EDX spectra at secondary phase sites shows that magnesium will deposit on the top of Fe containing intermetallic particles (Figure 4.4.5), but no magnesium peak can be found on the Si and SiO$_2$ surface in Auger spectra (Figure 4.4.6 and Figure 4.4.7). This indicates that Fe containing intermetallic particles, the same as the intermetallic in 15 % SiC$_p$/6061 Al MMC, act as cathodes in the micro-galvanic cell. Due to the oxygen reduction, magnesium ions can be trapped by locally high concentration of hydroxide ions and form Mg(OH)$_2$ deposition. Such a phenomenon does not appear on Si and black particles, which means that the over-potential for oxygen reduction at the semi-conductor or the insulator phase is very high. So these kinds of particles do not display the cathodic activity.

A long term corrosion test for 6061 Al was performed in neutral NaCl solution, and
the SEM micrographs at the same region for this specimen, taken before and after immersing for 191 hr, are presented in Figure 4.4.8. Through the examination of the two photographs we can find that a large number of pits appear as the result of immersion, and all pits occur around secondary phase particles. The pits are likely to be formed by micro-galvanic corrosion that is related with secondary phases, since the shapes of the pits are round circles. Point Auger and EDX analysis are performed on the secondary phases. Two kinds of particles that can induce the pits have been recognised, one is composed of Al, Fe and Si, the other is composed of Si and Mg. The photographs in Figure 4.4.8 show that one particle does not create a pit. Auger and EDX (Figure 4.4.9) spectra show that in such case probably a Si particle is the secondary phase. Although all of the Auger and EDX spectra present Si and Al peaks, a phase containing only Al and Si in 6061 Al cannot be found in the phase diagram. The aluminium signal may come from the surrounding matrix, since the particle is too small to collect a pure signal from it alone.
Figure 4.4.8 The SEM photographs for 6061 Al. Top: polished specimen, bottom: same region, but the specimen was immersed in 3% NaCl solution at pH value of 7 for 191 hr.

On the top part of Figure 4.4.10 two white particles and one hole-like black spot can be seen. The lower part of this figure is the same region as the top one, but
the specimen has been exposed in neutral NaCl solution for 191 hr. Comparing these two photographs, we can find that at the black spot develops a white particle. As mentioned before, the black spot always contains silica at the top surface that is recognized from the chemical shift of Si (KLL) peak. After corrosion, silica no longer exists on the top of white particle (Figure 4.4.11). The question is if the silica originally exists in the alloy? In general idea, silica is an insulator, and it is difficult to dissolve in neutral NaCl solution. If it wraps up the particle, the particle should no longer show cathodic performance. The experimental results show that the particles underneath silica also express cathodic property; this at least means that the silica does not cover the particles completely. Another possibility is that the silica exists as contamination. The secondary phases do not bond with the matrix alloy very well, the materials at the top of secondary phases were removed during the polishing process, and then some contamination came into the hole. The contamination may come from polishing process or during the period of storage in the desiccator since silica gel is used in the desiccator to keep the environment at low humidity. More careful experiments should be performed if we want to give an accurate explanation.
Figure 4.4.10  The SEM photographs for the specimen of 6061 Al before (top) and after (bottom) immersing in neutral NaCl solution.
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4.5 THE INTERMETALLICS IN SiC/6061 Al MMC

The SiC/6061 Al MMC is reinforced by eight layers of unidirectional SiC fibres. The detail of the fabrication process is not clear, but we know that it is processed by bonding eight 47% SiC/6061 Al monotypes with Cu interlayers. So the matrix contains much more copper than 6061 Al alloy and SiCp/6061 Al, which can be confirmed by EDX spectra collected at a matrix position (Figure 4.5.1).

Like the other two materials, some intermetallic particles exist in SiCp/6061 Al MMC (Figure 4.5.2). One kind of intermetallic particles is similar to the particles found in the matrix of SiCp/6061 Al MMC and 6061 Al alloy, which all contain Fe.
In order to compare the compositions of the two particles, EDX quantitative analysis was performed.

As mentioned in chapter 3, there are some deficiencies for EDX analysis of small particles due to the influence of the signal coming from matrix on the analysis result. The puzzle is even worse when quantitative analysis is performed. In order to get more reasonable results, a very thin specimen was prepared for TEDX analysis. The advantage of this method is that a purer signal from particles can be obtained if the specimen is thin enough, and no matrix alloy attaches on the particles. In this case the specimen preparation is most important.

The SiC$_p$/6061 Al MMC specimen was cut by ACCUTOM to get a thickness of less than 1 mm. The SiC$_p$/6061 Al sample is not easy to cut, either in parallel or in vertical direction to the axis of the fibres, so it was peeled by a knife. Mechanical polishing was carried out on this specimen to thin it to a few hundred micro-meters. At this stage, the specimen was still too thick to do TEDX analysis, since only the specimen with a thickness of a few ten nano-meters could meet the requirement of...
Chapter 4 Micro-galvanic corrosion cells in SiC/Al MMCs & Al alloy

Figure 4.5.2 Micrographs of SiC/6061 Al.

this technique. There are a few methods to get a thin specimen, such as electropolishing, chemical polishing, ion and atom milling and ultramicrotomy. The last method is mainly used in preparing polymer specimens in our laboratory. Electropolishing and chemical polishing are not suitable for composite materials. This is due to the fact that more than two phases are included in the materials, which are not dissolved at the same speed, especially the chemical properties of silicon carbide and aluminium are quite different. For these reasons the ion milling method was used in this project. The ion used here was argon, which was accelerated to a few keV. Atoms can be sputtered away, so the specimen is thinned. The specimen was rotated during thinning to prevent a ridged surface being developed. The sputtering was stopped when a small hole was generated on the centre of the specimen. By this means a large region of thin sheet was produced around the hole.

Quantitative EDX analysis was carried out on the EM 400 STEM SYSTEM, which
Figure 4.5.3 The EDX spectra of the Fe containing intermetallic particles in SiC/6061 Al MMC (left) and SiC/6061 Al MMC (right). The quantitative data come from these data.

was manufactured by Philips company. One important thing was to select the particles that could be analyzed. In order to get more accurate results, the interference coming from the matrix must be eliminated, only the particles at the edge of thin sheet were chosen for analysis, i.e. those particles that have less matrix attached to them. A series of EDX spectra were taken and quantitative results were calculated by computer program. Table 4.1 is the results collected from SiC/6061 Al and SiC/6061 Al MMCs. The data listed in this table are generated from the spectra that contain lowest concentration of aluminium (Figure 4.5.3): that means those with less interference coming from the matrix.

Table 4.1 The atomic concentrations of elements consisted in Fe containing particles in SiC/6061 Al and SiC/6061 Al MMCs

<table>
<thead>
<tr>
<th>elements</th>
<th>Al</th>
<th>Si</th>
<th>Cr</th>
<th>Fe</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC/6061 Al MMC</td>
<td>71.71</td>
<td>9.82</td>
<td>-</td>
<td>15.92</td>
<td>2.55</td>
</tr>
<tr>
<td>SiC/6061 Al MMC</td>
<td>77.2</td>
<td>7.57</td>
<td>5.71</td>
<td>8.65</td>
<td>0.88</td>
</tr>
</tbody>
</table>
Comparing the phases existing in 6061 Al (Table 2.2) and examining the atomic ratio of each element, the particles in SiCp/6061 Al MMC are probably Fe₃SiAl₁₂.
containing a little copper in substitution of Fe. For the particles in SiC/6061 Al MMC, some of the iron was replaced by chromium. The correct structure should be confirmed by electron diffraction results. A set of electron diffraction patterns was collected, but since there are no standard data for these particles in the literature, the attempt was given up.

In the matrix of SiC/6061 Al MMC, there exist the other two phases. Figure 4.5.4 and Figure 4.5.5 present the point analysis results at the other two particles' position. Comparing the possible phases existing in 6061 Al, we can find that one particle is probably a Si phase, the other one is much more like a CuAl$_2$ phase.

![SEM micrograph of SiC/6061 Al MMC which was exposed in neutral NaCl solution for 191 hr.](image)

**Figure 4.5.6** SEM micrograph of SiC/6061 Al MMC which was exposed in neutral NaCl solution for 191 hr.

After SiC$_f$/6061 Al MMC specimen was exposed to a neutral NaCl solution for 191 hr, it could be found that some particles could induce pits around them but some did not (Figure 4.5.6). Careful examinations were performed on those particulates. Combining the SEM micrograph and Auger/EDX point analysis, it can
Chapter 4 Micro-galvanic corrosion cells in SiC/Al MMCs & Al alloy

Figure 4.5.7 Auger/EDX maps show that Cu containing particulates can induce pits. Fe containing particulates do not show the property of micro-galvanic corrosion. The specimen is SiC/6061 Al MMC.

be found that Si particulates were much more stable, no holes were found around them. Figure 4.5.7 shows the Auger/EDX maps and a secondary electron image for the specimen of SiC/6061 Al MMC that had been exposed in neutral NaCl
Figure 4.5.8 Auger/EDX maps for the specimen of SiC/6061 Al MMC which was exposed in 0.1 M MgCl₂ solution for 20 min. Solution for 20 min. The secondary electron image shows that one small particle can darken the surrounding matrix. Previous experience told us that corrosion has happened there. The EDX map shows that particle is Cu-containing intermetallic. On the contrary, no sign indicates that Fe containing intermetallics are related to
micro-galvanic corrosion.

Unlike the Fe containing particulate existing in SiCp/6061 Al MMC, the particulates that are similar but do not bring on pits in SiCp/6061 Al MMC are shown in Figure 4.5.7. In order to confirm the lack of cathodic activity, the ion decoration method was used. The SiCp/6061 Al MMC specimen was exposed to 0.1 M MgCl₂ solution for 20 min, soaked in Milli-Q water for two seconds, and then dried it by standing on a tissue. Figure 4.5.8 presents the Auger and EDX maps acquired from this specimen. Although the quality of this set of maps is not good, it still shows that magnesium and oxygen signal are not high at the top of intermetallic particulate. That means this intermetallic has a very low cathodic activity.

Cr in this intermetallic seems play an important role on anti-corrosion performance. The mechanism may be the same as with the stainless steel, that means Cr is involved in forming a passive film on the top of intermetallic particulates. This film has semi-conductor properties but it has much higher passivation property.

### 4.6 THE EFFECT OF SiC PARTICLES IN SiCp / 6061 Al MMCs

In the previous sections, the effect of different intermetallic particles in the corrosion cells was discussed, which showed that some intermetallic particles could form micro-galvanic cells with Al matrix, and some could not. In this part of work the attention was focused on the reinforcement in the MMCs: it is also the matter of interest to the MMC's designers.

There are 15 % silicon carbide particles in the SiCp / 6061 Al MMCs. When the polished specimen was exposed to neutral NaCl solution for 20 min, it seems that nothing happened around or on the SiC particulates. This phenomenon can be found from SEM photographs in section 4.2 (Figure 4.2.2). A long term exposure
to neutral NaCl solution was performed on the same specimen, the SEM micrograph is displayed in Figure 4.6.1. The centre big halo is induced by the intermetallic particle which forms a micro-corrosion cell with the surrounding aluminium matrix. Some small intermetallic particles can also make the matrix form small halos. This shows no difference with previous results. Regardless of intermetallic particles, the concentration was focused on the SiC particles. From the micrograph, it was found that the matrix next to some of SiC particulates was corroded and cracks can be found near the SiC particulates. The cracks were related to the dry corrosion products formed there. The difference between intermetallic and SiC particulates is that the morphologies around them after corrosion are quite disparate. There are normally no circular halos formed around SiC particulates of the form always found around intermetallic phases. From the SEM micrograph, it is difficult to get an idea whether the SiC particulates can form micro-galvanic cells with the matrix or not.

Figure 4.6.1  Micrograph of SiCp/6061 Al after 190 hr exposure in 3% NaCl solution, pH 7.2.
Examination of cathodic activity of SiC particulates was carried out by ion decoration. We had shown, in section 4.2, the Auger and EDX maps for the specimen which was exposed in 0.2 M MgCl$_2$ solution. Magnesium can be found on the top of intermetallic particulate, but it did exist on the top of SiC phases. A much higher concentration of MgCl$_2$ solution was used to examine the cathodic activity of the SiC particulates. The concentration used in this set of experiment is 1 M, so that when the pH value rises to 8.6 at cathodic regions, Mg(OH)$_2$ will be deposited. Figure 4.6.2 is a set of Auger and EDX maps for the SiC$_p$/6061 Al MMC specimen that was exposed in 1 M MgCl$_2$ solution at pH value of 8.2 for 20 min. By comparing the EDX silicon map with the Auger magnesium maps, we can find that there is no Mg(OH)$_2$ deposition on the top of SiC particulates. The concentration of magnesium and pH value of the solution used here are quite high, they are approaching the solubility product of Mg(OH)$_2$. That means if there is any galvanic current between SiC particulates and Al matrix, the current must be very small.

**Figure 4.6.2** Auger maps show no magnesium deposition on the top of SiC particulates after the SiC$_p$/6061 Al specimen was exposed in 1 M MgCl$_2$ solution at pH value of 7 for 20 min.
The most possible corrosion problem related with SiC particulates is crevice corrosion since these crevices are angular, following the shape of the SiC particulates and do not present the shape of a ring which is characteristic of the micro-galvanic cells. The reason for this crevice corrosion is probably the difficulty of sustaining a protective film across the phase boundary; as such the phenomenon is classic in its cause. There are also some cases of a small half-halo attached to the SiC. A small impurity particle present at the interface is probably the main factor.

4.7 THE CORROSION EFFECT OF SiC FIBRE IN Al MMC

4.7.1 Immersion Test

The most popular corrosion test is simply to expose the specimen into the solution of interest. In order to examine the effect of SiC fibres, the first experiment was to immerse the SiC/6061 Al MMC specimen into a 3% neutral NaCl solution. To get a distinguishing result, the exposure time used here was about 1 week. Figure 4.7.1 is the SEM micrograph for the SiC/6061 Al MMC specimen after corrosion. The low magnification photograph shows that a cracked ring is created around the fibres. The high magnification photograph shows that the matrix surrounding the fibre is dissolved as a result of corrosion.

The result of the previous section shows that there is nearly no galvanic current between SiC particulates and Al matrix. From the morphology of the specimen after corrosion shown in Figure 4.7.1, the corrosion of aluminium is most probably related to the SiC fibres. More detailed consideration to this inconsistency is given below.
Figure 4.7.1  SEM micrography of the SiC/6061 Al MMC, which was exposed in 3% neutral NaCl solution for 190 hr.

4.7.2 The Structure of SiC Fibre

There are several layers existing in SiC fibres as shown in the SEM micrographs
Figure 4.7.2  SEM micrographs of polished SiC/6061 Al MMC specimen, which show different structures existing in the fibres.

(Figure 4.7.2). Auger and EDX analysis (Figure 4.7.3) was performed on the points marked on the fibre. The Auger spectrum on point ‘a’ shows that only carbon exists in the black fibre core, the EDX spectrum shows that there is some sulphur contained in the core. At points ‘b’, ‘c’ and ‘d’ only silicon ($K_{aB}$) peak can be found from the EDX spectrum, and only the carbon (KLL) peak can be found from the Auger spectrum, this correlates with SiC. The bottom of Figure 4.7.3 are the spectra collected from the interface of SiC fibre and Al matrix. C, O, Al and Si can be found from Auger spectrum, Al, Si and a small amount of Cu appear in the EDX spectrum.

In order to obtain more information on the interface of the fibre and the Al matrix, a WDX lineprofile was acquired by JEOL JXA-8600 superprobe across the matrix/SiC fibre region. Since this instrument is equipped with a crystal spectrometer, it is possible to analyze carbon. The lines shown in Figure 4.7.4, are Si, C, and Al respectively from top to bottom. Silicon signal is low in the matrix
Figure 4.7.3 Auger and EDX spectra collected on the points that were marked on the fibre. Top row was acquired from point A, middle row expressed the composition of point b, c and d, the bottom row was acquired on point e.
Figure 4.7.4 WDX line profile across the outside coating of SiC fibre. Top: Si, Middle: C. Bottom: Al.

area, increases a little bit at the coating position, and finally gets to the highest value that is associated with SiC. On the contrary, aluminum is high at the matrix position and begins to decrease at the coating region. The carbon signal is high at
Figure 4.7.5 XPS images of Si(2p), carbide (C1s) and graphite (C1s). The images were collected from the polished SiC/6061 Al MMC.
the coating region, which is about 1.1 μm in width.

![XPS spectrum](image)

**Figure 4.7.6** XPS spectrum for C 1s peak acquired from polished SiC/6061 Al MMC specimen after 60 seconds etching.

The XPS imaging technique was used to check the chemical states of the SiC fibre. The main advantage of XPS is its high energy resolution, so the chemical state information can be obtained from XPS spectra, and furthermore the distribution on the surface can be revealed from XPS images. Fisons Instruments - ESCALAB 220i XL was used to map out the Si(2p) and C(1s) for carbide and graphite (Figure 4.7.5). The X-ray source used in the set of maps is Al kα. The window setting for carbide is at the binding energy of 283.3 eV, and 284.5 eV for the graphite images. The spatial resolution of this instrument is down to 1 μm. As shown in Figure 4.7.5, C1s, for graphite, distributes at the carbon core position, and it can also be found outside the coating position. C1s, for carbide, can be found all around the fibre. Although it seems that more carbide is contained in the carbon core as shown in the image, this may partly be caused by the real carbide
existing in the core, and partly caused by the overlaps of carbide peak and graphite peak since the binding energy of those two peaks are close to each other (Figure 4.7.6). Except for the core position, carbide present at other places relates to the Si 2p image: This is the place where silicon carbide is located.

Comparing the micrograph and the data collected from the fibre with the literature, this fibre is very similar with the one which is called SCS-6 fibre. Ning and Pirouz drew a diagram of the structure of SCS-6 fibre which is shown in Figure 4.7.7. The fibre contains a carbon core, which is deposited with different grain sizes of SiC by chemical vapour deposition. Between the carbon core and SiC, there is a layer of inside coating which mainly composed of pyrolytic graphite. A carbon layer is coated outside of SiC and slightly enriched with silicon on its surface.

The silicon coated on the outside of the fibre is used to prevent the reaction of the fibre with Al matrix to form AlC₃. The literature shows that silicon is slightly enriched on the outside surface of coating, but the WDX linescan does not show
this result. The possible reason for this is that this layer is very thin, WDX does not have such high spatial resolution.

4.7.3 Ion Decoration to Identify the Micro-galvanic Cell between Fibre and Al Matrix

In the last section, the structure of the fibre was determined by Auger, XPS, EDX and WDX techniques. As a general idea, graphite has a very low overpotential for oxygen reduction, it could be very dangerous if graphite is contained in active metals, such as Al. In SiC/6061 Al MMC, the graphite core was separated from the Al matrix by a very thick SiC layer, we will find out if it is still very active or not. The outside coating, as mentioned in the literature, contains some silicon, it may also reduce the activity of the graphite. The following experiments are designed to find out the answers.

Carbon Core in the SiC Fibre
MgCl₂ solution was successfully used to identify intermetallic particles in SiC particle reinforced 6061 Al alloy as cathode particles. The same method is used in SiC fibre reinforced 6061 Al alloy. Figure 4.7.8 is the Auger and EDX maps for the SiC/6061 Al specimen which has been exposed to 1 M MgCl₂ solution at pH value of 8.17 for 20 min. Aluminium and silicon signals for both Auger and EDX maps are complementary to each other. Aluminium signal is indicated in the matrix position, while silicon signal is where the SiC fibre is. In the centre of SiC fibre, which should be the carbon core position, carbon signal is absent. On the contrary, the Auger oxygen is very strong at the carbon position, it is even higher than the intensity from the matrix, corresponding to the aluminium oxide film. Both chlorine and magnesium signal are high in the fibre region, but magnesium is more concentrated on the carbon core position, while chlorine is almost uniformly distributed on the fibre surface. Although chlorine exists on the centre
Figure 4.7.8 Auger and EDX maps for the SiC/6061 Al specimen which was immersed in 1 M MgCl$_2$ solution at pH value of 7 for 20 min.

core at a little higher concentration than in other places, it is not as high as the magnesium which exists on the core surface. All of these mean that the carbon core is covered by magnesium and oxygen which is most possibly in the form of Mg(OH)$_2$, and some MgCl$_2$ mingles in the Mg(OH)$_2$ deposition. This result is due
the fact that oxygen can be reduced at the carbon core surface and the concentration of hydroxide ion at this area increases to the value which can make magnesium ions deposit. A low intensity of aluminium can also been observed at the core position, that is the concentration of aluminium and hydroxide ions also reach the solubility product of Al(OH)$_3$ at the core area. As the concentration of dissolved aluminium is not high enough to provide enough ions to the cathodic region, the intensity of aluminium is not as high as magnesium in this area. Copper is distributed all over the matrix region, and some iron particles also exist in the matrix, most of them located at boundary positions.

Figure 4.7.9 Scatter diagram used for Mg, Cl and O Auger maps in Figure 4.7.8.

Figure 4.7.9b is the scatter diagram used for the Auger magnesium and chlorine maps. The blue circle corresponds to the position where both magnesium and chlorine exist, it seems that MgCl$_2$ is much more likely to be absorbed on the fibre surface than the matrix. The yellow region corresponds to a relatively high magnesium phase, say Mg(OH)$_2$, which relates to the cathodic reaction.
Figure 4.7.9a shows the scatter diagram (right) of oxygen against magnesium. The yellow circle correlates to the high Mg and high O Signal, which is located on the carbon core position as displayed in the rebuilding map (left). The green circle includes the pixels that have very low Mg intensity and relatively high O intensity, these pixels are related to the Al matrix position. The high oxygen signal identifies the aluminium oxide existing on the Al matrix surface, the low Mg intensity shows the absence of magnesium salts on matrix surface. The pixels with low O and medium Mg intensity were drawn in the blue circle, and are located at SiC fibre positions. That means that some Mg salts are absorbed on the SiC surface.

As mentioned before, high concentration of chlorine and magnesium can be found in carbon core area. The explanation is that the Mg(OH)\textsubscript{2} and MgCl\textsubscript{2} are all existing at that region. An image processing method is used to confirm this. Daud (1985) has measured the sensitivity factors for Cl and Mg by using VG MA 500 with standard specimen, the data is listed in Table 4.2. In this case the atomic ratio of Cl/Mg from AES result can be given by

\[
\frac{\text{Cl}}{\text{Mg}}_{\text{AES}} = \frac{f_{\text{Mg}}}{f_{\text{Cl}}} \cdot \frac{A_{\text{Cl}}}{A_{\text{Mg}}}
\]

Where \(f_{\text{Mg}}\) and \(f_{\text{Cl}}\) are the Auger sensitivity factors, \(A_{\text{Mg}}\) and \(A_{\text{Cl}}\) are the peak areas of Mg and Cl obtained in AES analysis. There are two magnesium compounds present on the specimen surface. If chlorine salt on the specimen surface is only in the structure of MgCl\textsubscript{2}, then the pure Mg signal coming from the Mg(OH)\textsubscript{2} can be obtained by using the following equation:

\[
[Mg]_{\text{Mg(OH)2}} = [Mg]_{\text{total}} - 2 \cdot \frac{f_{\text{Mg}}}{f_{\text{Cl}}} \cdot [Cl]_{\text{total}}
\]
Table 4.2 AES sensitivity factor for Mg and Cl
(after Daud 1985)

<table>
<thead>
<tr>
<th>Element</th>
<th>Auger Peak (eV)</th>
<th>Sensitive factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>181</td>
<td>0.72</td>
</tr>
<tr>
<td>Mg</td>
<td>1186</td>
<td>1.54</td>
</tr>
</tbody>
</table>

Unfortunately MgCl₂ is not the only form of chlorine salt existing in the deposit, the chlorine salts can be MgCl₂, NaCl or AlCl₃ etc.. So if the sensitivity factors are used in subtracting the influence of chlorine salts, there will be no Mg Auger signal at all. So a relatively pure Mg(OH)₂ signal is obtained by subtracting Cl the Auger signal from the Mg Auger signal, and then we can get Figure 4.7.10 which shows...
the region of the existing Mg(OH)$_2$. By subtracting the Mg Auger signal from Cl Auger signal, we can get chloride salt which does not contain magnesium. Comparing the regions of fibre with matrix, chloride salts seem much more likely to be adsorbed on the fibre surface. There is also much more chloride existing at the inner coating region as shown in EDX chlorine map in Figure 4.7.8: that may due to the softness of the pyrolytic graphite. When the specimen was polished, the inner coating layer was removed much more than in other places on the fibre.

Imaging XPS was used to identify the ion deposition on the cathodic area. Mg (KLL), Al (2p) and C (1s) images were acquired and treated by peak-background, and are shown in Figure 4.7.11. The result is similar to the Auger maps, which shows the magnesium signal to be very high at the position of the centre core and aluminium can also be found at the core region. That means the concentration of OH$^-$ is higher at the core position than at other places, exceeding the solubility products of Mg(OH)$_2$ and Al(OH)$_3$, which are then deposited on the core region. Carbon signal is lower at the core position: this is quite different to the clean specimen as shown in Figure 4.7.5, and is due to the deposits that cover that region.

The Interface Between Fibre and Al Matrix
The intensity of magnesium and chlorine are also high at the fibre and matrix interface as displayed in the Auger maps of Figure 4.7.8, but this is not clearly shown on the XPS image for the element Mg. This is due to the high spacial resolution of SAM. In order to know the distributions in detail, a set of high magnification maps from another fibre in the same specimen was acquired (Figure 4.7.12). Magnesium intensity is high at the coating area, but chlorine is not high at that position. This indicates that the outside coating is also acting in the role of cathode. The cathodic effect of the outside coating, as comparing with carbon core, is not very strong, since both magnesium and oxygen intensity are not as high as on the surface of carbon core. That is probably due to the fact that outside coating is not pure carbon. Silicon existing in this layer reduces the
Figure 4.7.11  XPS images of Mg (KLL), Al (2p) and C (1s). The specimen was treated by exposure in 1 M MgCl$_2$ solution at pH value of 8.17 for 20 min.
Figure 4.7.12 Top: Auger maps for the SiCp/6061 Al specimen which was immersed in 1 M MgCl₂ solution at pH value of 7 for 20 min. Bottom: processed image by subtract aluminium metal from aluminium oxide.

Figure 4.7.12 gives two Auger aluminium maps, one is for aluminium metal and the other is the aluminium oxide map, as the kinetic energies have 7 eV difference in Auger spectra. A low intensity of aluminium metal near the fibre can be observed. A mathematical process was used for these two maps to subtract aluminium metal from aluminium oxide. A ring is displayed near the fibre. This phenomenon outlines the area acting as anode, i.e., anodic effects make the oxide
Figure 4.7.13 Three images are overlapped together. Red: Auger aluminium oxide map is subtracted by aluminium metal map, green: Auger magnesium map, blue: EDX silicon map.

layer becomes much thicker than in other places. Through overlapping three images, which are Auger Al(O)-Al(M), Auger Mg and EDX Si, we can find that aluminium oxide is enriched near SiC fibre, magnesium is concentrated on the coating region, where silicon and aluminium oxide are all low (Figure 4.7.13). This picture shows clearly the region of cathode and anode.

In order to confirm the effect of the outside coating of the fibre, the specimen was fractured in parallel to the fibre direction, and then exposed in 1 M MgCl₂ solution at pH value of 7 for 10 min. Figure 4.7.14 are the Auger and EDX maps of this specimen and Figure 4.7.15 is the sketch map which shows the region of the Auger and EDX maps in Figure 4.7.14. The secondary electron image shows that the outside coating is still maintained on the fibre in some areas. At the place where the coating exists, the oxygen and magnesium signals are higher than in other places, which means the cathodic reaction happened at the region with the carbon
The Auger chlorine map shows that Cl distributes uniformly on the fibre surface, but the concentration is higher at the interface between fibre and matrix. Image processing (Figure 4.7.16) is used to highlight the enriched regions of coating.
corrosion products and \( \text{Mg(OH)}_2 \) by using equations listed on the following:

\[
[Mg]_{\text{Mg(OH)}_2} = [Mg]_{\text{total}} - 2 \cdot \frac{f_{\text{Mg}}}{f_{\text{Cl}}} \cdot [\text{Cl}]_{\text{total}}
\]

\[
[\text{Cl}]_{\text{otherform}} = [\text{Cl}]_{\text{total}} - \frac{1}{2} \cdot \frac{f_{\text{Cl}}}{f_{\text{Mg}}} \cdot [Mg]_{\text{total}}
\]

**Figure 4.7.15** The sketch map shows the region of Auger and EDX maps in Figure 4.7.14.

Figure 4.7.16 shows magnesium coming from \( \text{Mg(OH)}_2 \) distributes on the outside coating region, and chlorine coming from the corrosion products distributes on Al matrix region.

From above results, we know that carbon core, carbon coating and intermetallic
particles can act as cathodes. The carbon coating and intermetallic particles are in directly contact with aluminium matrix, and they easily form a galvanic cell with the matrix. As for the carbon core, it is separated by SiC from the matrix. The experimental presentation shows that oxygen can be reduced at this region. In this case, electrons must pass through the whole silicon carbide region. The silicon carbide acts as a conductor in this kind of galvanic cell although it is a very poor conductor.

4.7.4 Estimation of Cathodic Current Densities on Carbon Core and Carbon Coating

In section 4.3, cathodic current density was estimated by the method of magnesium ion decoration. The same method is used on the carbon core and carbon coating of SiC fibre.

As discussed before, the first step is to examine the critical concentration for the magnesium precipitation. The SiC/6061 Al MMC specimen was exposed in MgCl₂ solutions at concentrations of 0.2 M, 0.1 M, 0.01 M, and 0.001 M for 10 min. After
a short washing time, the specimens were subjected to Auger/EDX analysis. Mg(OH)$_2$ can be found at carbon core and carbon coating position when the concentration of MgCl$_2$ is 0.1 M. This indicated that the critical concentration for the magnesium precipitation was between 0.01 M to 0.1 M.

It is not easy to determine the diffusion distance of hydroxide ion. Assuming the diffusion distance, $\delta$, is the twice of the thickness of coating layer when the carbon coating layer as a cathode, and $\delta$ is 2$r$ when the carbon core act as a cathode where $r$ is the radius of carbon core, the cathodic current density can be calculated by using Eq 4.7 if the plane sheet diffusion model is used. The results are listed in Table 4.3.

<table>
<thead>
<tr>
<th></th>
<th>$\delta$ (µm)</th>
<th>[Mg$^{2+}$] (M)</th>
<th>I (µA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-coating</td>
<td>2.4</td>
<td>0.01-0.1</td>
<td>887-280</td>
</tr>
<tr>
<td>C-core</td>
<td>38</td>
<td>0.01-0.1</td>
<td>56-17</td>
</tr>
</tbody>
</table>
Chapter 5  Electrochemical Experiments

All the experiments above used surface analysis or electron microscopy techniques to investigate the micro-galvanic corrosion cells associated with MMCs. The work in this section will focus on the individual components in the composites, and the study of their electrochemical properties.

5.1 SPECIMENS

Several materials were investigated in this set of experiments, including 6061 Al and 15% SiCₚ / 6061 Al MMC. Due to the difficulty of preparing specimens, SiCₚ/6061 Al MMC was not included here. In last chapter, we found that the intermetallic particulates were drawn into the micro-galvanic corrosion cells. The intermetallic particulates mainly contain Fe, so commercial Fe, which contains 99% Fe, and an Al-8Fe-Ni alloy that contains a large amount of Al₃Fe intermetallic was used to provide relevant electrochemical data independent of the MMC.

The specimen for metal and MMC was cut to 10×10 mm, and ground with 320, 500, 1000, 4000 ground paper, and then polished to 1 μm. OP-S was used for the final polishing. Before the electrochemical experiments, specimens were cleaned with acetone (analytical grade) and Milli-Q water.

To investigate the role of the reinforcement in the galvanic-corrosion cell, several kinds of SiC fibres were prepared. The first fibre we selected was SCS-6 fibre, which has a similar composition to the fibre used in SiCₚ/6061 Al MMC. Another fibre selected was a SiC fibre without a surface coating, so the SiC is exposed. This
fibre is very important for the examination of the corrosion effect of SiC. The third one we have used is the SiC fibre with a pure carbon coating, it was used to investigate the cathodic effect of carbon. The fourth one was SiC fibre coated with TiB₂, as is usually used in Ti MMCs. Two kind of carbon fibres, sized and un-sized, were also investigated by electrochemical experiments.

The surface morphology of those fibres was examined by using SEM, which is shown in Figure 5.1. SCS-6 fibre is smoother than the other three SiC fibres, we can also find several coating layers from SEM micrographs of the broken end. The surface structure of SiC fibre coated with TiB₂ is also fine as well, but it is not as fine as SCS-6 fibre. Since these two fibres are commercially available, the manufacturing conditions are much better refined than the other two fibres. The SiC fibre without coating has a much rougher surface, and no coating layer can be seen, as shown in the photograph. The roughness of SiC fibre with C-coating is nearly the same as SiC fibre without coating, but we can find the coating layer in an image of the broken end.

Table 5.1 The diameters of the four type of SiC fibres and two carbon fibres

<table>
<thead>
<tr>
<th>Type of fibre</th>
<th>Diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCS-6</td>
<td>139.4</td>
</tr>
<tr>
<td>Un-coated SiC fibre</td>
<td>107.5</td>
</tr>
<tr>
<td>SiC fibre with C-coating</td>
<td>107.5</td>
</tr>
<tr>
<td>SiC fibre with TiB₂ coating</td>
<td>105.3</td>
</tr>
<tr>
<td>Sized carbon fibre</td>
<td>7.4</td>
</tr>
<tr>
<td>Un-sized carbon fibre</td>
<td>7.4</td>
</tr>
</tbody>
</table>

All of these fibres had different diameters, as are listed in Table 5.1. These
data are used to determine the area of the electrode when current density is measured during the electrochemical experiments.

The surface composition of the fibre directly affects the electrochemical reaction.
Figure 5.2 Auger and EDX analysis on the surface of four types of fibres.
In order to confirm the composition of each fibre, Auger and EDX analysis (Figure 5.2) were performed on the outside surface of the fibres. As reported, SCS-6 fibre is enriched in Si on the outer surface: we can find Si (KLL) peak in the Auger spectrum, but the peak is not as high as the same peak found in the Auger spectrum taken from the SiC surface. The EDX spectra of the two fibres are similar in that only the Si (Kα) peak can be found, but the counts for un-coated SiC fibre are much higher than the counts for the SCS-6 fibre. That means carbon is the dominant element on the surface of SCS-6 fibre. An O (KLL) peak can be found almost in every Auger spectrum, it may, partly, come from the oxidation of the fibre surface, or partly from the contamination. An interesting thing is that the oxygen signal is very low on the C-coated fibre, this may mean that most of the oxygen signal comes from the oxidation of the SiC surface. The EDX spectrum acquired from the C-coated fibre shows that there is a small amount of Cl in the coating. No Cl peak can be found from Auger spectra of the same fibre, which means the Cl is not caused by storage contamination, it comes from the CVD (chemical vapour deposition) process. A strong B(KLL) peak is displayed in the Auger spectrum acquired from TiB$_2$-coated fibre, but the Ti (LMM) signal is relatively low as compared with the B signal. The coating on the surface may be non-stoichiometric TiB$_2$ since the Ti Auger signal is normally more intense than the B Auger signal (Davis et al, 1976). Ti (Kα, Kβ) peaks are clearly shown in the EDX spectrum.

5.2 ELECTROCHEMICAL EXPERIMENTAL FACILITY

Electrochemical experiments were carried on the Model 173 Potentiostat / Galvanostat, which is produced by EG&G Princeton Applied Research. The experimental condition and data acquisition are controlled by an Apple II computer through the Model 276 interface. The computer software used in this project is model 332 "SOFTCORR" corrosion software (Figure 5.3).
The electrochemical cell is made of glass, the layout is displayed in Figure 5.4. This cell can meet the normal requirement of the electrochemical experiments. It has a good cell volume, and the electrolyte is easily to be removed from the cell. Aeration or de-aeration can be achieved with perforated tubes. The main disadvantage of this cell is that the auxiliary electrode is placed opposite the surface of the working electrode, this will result in non-uniform current flow and the current density will be greatest at points of minimum separation. The auxiliary electrode used here is a square piece of platinum sheet with an area of 2 cm² on one side. A saturated calomel electrode is used as reference electrode.
A specially designed specimen holder is used for metal and MMC specimens. The materials used for the specimen holder is polytetrafluoroethylene (PTFE), which has good insulating properties in many corrosion environments. The holder can accommodate a 10×10 mm square specimen with a 1.2 mm thickness. A PTFE gasket with inner diameter of 7.98 mm allows a 0.5 cm² exposure area of the specimen (Figure 5.5).

Several structures are contained within the transverse section of fibre, which would make it difficult to obtain the electrochemical properties of a single phase if this is used as working electrode surface. Instead, the outside surface of the fibre was investigated in this study, where only one phase exists for each kind of fibre. The layout of the fibre electrode is displayed in Figure 5.6. One end of the fibres is
sealed with lacomite, which avoids the influence of the other phases. The other end is linked with a copper wire, silver dag is used for good conductivity. At this end, the copper wire, silver dag and part of the fibres were covered by lacomite. The area, A, of the working electrode can be calculated through the diameter of
the fibre, the length of the electrode and the number of fibres used in one electrode:

\[ A = \pi \cdot d \cdot l \cdot n \]

where \( d \) is the diameter of one piece of fibre, \( l \) is the length of the electrode, \( n \) is the number of fibres used in the fibre electrode. Normally 12 pieces of fibres are used in each electrode, and the length is 22-26 mm.

\[ \text{5.3 RESULTS AND DISCUSSION} \]

\[ \text{5.3.1 Potentiodynamic Polarization} \]

\[ \text{Matrix alloy and the SiC}_p \text{ MMC - bulk materials} \]

The potentiodynamic polarization curves for 6061 Al alloy and 15 \% \( \text{SiC}_p / 6061 \) Al MMC in 3 \% NaCl solution, which is open to air, are shown in Figure 5.7. The scanning rate is 0.2 mV/sec. These curves show that the polarization behaviour of the composite and alloy are similar. The anodic current density for \( \text{SiC}_p/6061 \) Al is only a little larger than that of Al alloy, cathodic current densities for both \( \text{SiC}_p/6061 \) Al and Al alloy are nearly the same. In the 0.1 N NaCl solution which is open to air, the pitting potentials of 6061 Al and \( \text{SiC}_p/6061 \) Al MMC are less than 10 mV positive to the corrosion potentials as reported by Trzaskoma (1983), so the passive region can not be found in the polarization curves.

Table 5.2 lists the PARCalc Tafel analysis results, which shows that the corrosion potentials and corrosion currents for 6061 Al alloy and 15\% SiC/6061 Al MMC are nearly the same. The program of PARCalc Tafel analysis is included in the model
Figure 5.7 Potentiodynamic polarization curve for 6061 Al alloy and SiCp/6061 Al MMC in quiescent 3% NaCl open to air. The pH value is 7.

332 "SOFTCORR" corrosion software. The theory of PARCalc is as following. For the simple electrode reaction, the polarization curve can be expressed by the Stern-Geary equation.

$$I(E) = I_{corr} \cdot \left(10^{\frac{E-E_{corr}}{B_0}} - 10^{\frac{E-E_{corr}}{B_0}}\right)$$

PARCalc uses a $\chi^2$ minimization technique to find the values of the Tafel constants, corrosion potential, and corrosion current that best represent the experimental data. The calculation is automatically performed by computer, and it will terminate when the change in $\chi^2$ is less than 5%. The values of $\chi^2$ appear large in Table 5.2, which probably means, that the reaction of the electrode is not simple, passivation has occurred on the Al surface.
Table 5.2 The results of PARcalc Tafel analysis

<table>
<thead>
<tr>
<th></th>
<th>6061 Al alloy</th>
<th>SiCp/6061 Al MMC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>E (I=0) (mV)</strong></td>
<td>-702.47</td>
<td>-712.25</td>
</tr>
<tr>
<td><strong>Cathodic Tafel βc (mV)</strong></td>
<td>2598.47</td>
<td>1018.64</td>
</tr>
<tr>
<td><strong>Anodic Tafel βa (mV)</strong></td>
<td>53.61</td>
<td>49.46</td>
</tr>
<tr>
<td><strong>I_{corr} (µA/cm²)</strong></td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td><strong>Corrosion Rate (MPY)</strong></td>
<td>1.09</td>
<td>1.08</td>
</tr>
<tr>
<td><strong>χ²</strong></td>
<td>630.97</td>
<td>675.25</td>
</tr>
</tbody>
</table>

SiC fibres

Cathodic polarizations tests were performed on the fibre specimens in neutral 3% NaCl solution over a scan region of -900 to 0 mV (SCE). During scanning, the solution is opened to air. The scan rate is 0.2 mV/sec. In neutral NaCl solution the cathodic current measured from fibres is due to oxygen reduction.

\[
O_2 + 2H_2O + 4e = 4OH^- 
\]

Figure 5.8 shows the cathodic polarization curves of four kind of fibres. The uncoated SiC fibre, which has pure SiC exposed on the surface, can support oxygen reduction, but the cathodic reaction current density is very small. The fibre with pure carbon coating can support the largest cathodic current density. The surface of SCS-6 fibre contains some Si, but the concentration of Si is not as high as contained in stoichiometric SiC, the cathodic current density is nearly the same as the fibre with carbon coating. TiB₂ coating can effectively reduce the cathodic
Figure 5.8 Cathodic polarization curve for the fibre specimens. 1: un-coated SiC fibre, 2: SiC fibre with TiB$_2$ coating, 3: SCS-6 fibre, and 4: C-coated SiC fibre.

Current density on the fibres, but it is not as low as on SiC surface.

Polarisation diagrams for 6061 Al in neutral 3 wt% NaCl solution open to air are compared with the cathodic polarisation curves of un-coated fibre, SCS-6 fibre and C-coated fibre. As shown in Figure 5.9, the cathodic current density supported by un-coated SiC fibre is less than the cathodic current density on 6061 Al alloy. This means that the uniform corrosion rate for 6061 Al alloy is larger than the galvanic corrosion rate between SiC and 6061 Al alloy. Therefore there is no basis for galvanic interaction between the SiC and the matrix alloy in the MMC. On the contrary, the SCS-6 and C-coated fibre can support a larger cathodic current density. This means that the oxygen dissolved in the solution is much more likely to reduce on the pure carbon surface or the carbon containing silicon. The pure C-coating outside the SiC fibre may have the same cathodic polarisation...
performance as that of the carbon core in the SiC fibre, that is why a micro-galvanic corrosion cell can be found between the carbon core or the outside coating and the Al matrix in SiC fibre reinforced 6061 Al MMC. This electrochemical experiment result confirms our previous conclusions based on the surface analysis techniques.

By using the mixed potential theory, the total cathodic current is equal to the total anodic current. In the simplest situation, when the anodic area is equal to the cathodic area, the galvanic current between SCS-6 fibre or C-coated fibre and 6061 Al alloy can be found from the polarisation curves, the value of galvanic current density is about 20 μA/cm². In the real situation, the anodic area is larger than the cathodic area, this will be discussed later.
Comparison of polarisation curves for 6061 Al alloy and TiB₂-coated fibre (Figure 5.10) shows that the TiB₂ coating surface can support a larger cathodic current density than 6061 Al alloy. If this fibre is used in aluminium MMC, galvanic cells will be formed between fibres and matrix, but the corrosion current is much less than that which happens between SCS-6 fibre and Al. Supposing the anodic area is equal to the cathodic area, the galvanic current density is only about 5 \( \mu A/cm^2 \). In practice the TiB₂-coated fibres are only used in titanium MMCs.

**Carbon fibres**

The carbon fibres have different electrochemical performance depending on whether they are sized or un-sized as shown in Figure 5.11. The un-sized carbon fibre can support a cathodic current which is much higher than the carbon fibre...
that is sized. Another difference is that a small peak appears on the cathodic curves for the un-sized carbon fibre at -300 mV (vs SCE), this phenomena means that some component in un-sized fibre can be reduced at this electrode potential.

![Cathodic polarisation](image)

**Figure 5.11** Cathodic polarisation for 1: 6061 Al alloy, 2: sized carbon fibre, and 3: un-sized carbon fibre.

**Iron and intermetallic**

In the last chapter, we found that micro-galvanic corrosion happened between intermetallic particles and Al matrix. Most of the intermetallic particulates contain Fe, so the cathodic polarisation performance of pure Fe is investigated here. Figure 5.12 includes three potentiodynamic polarisation curves, which are 6061 Al alloy, pure Fe, and SCS-6 fibre. The cathodic current densities supported on Fe and SCS-6 fibre are nearly the same, which are all diffusion controlled by the reduction of oxygen. Galvanic corrosion can certainly happen between Fe and Al
As Fe is only one component in the intermetallic compound, there is a comparatively large difference from reality in using the galvanic current between the Fe and Al matrix to determine corrosion rates. In order to simulate more closely the real situation of the micro-galvanic cell in Al MMC and Al alloy, an attempt was made to get the polarization curve of pure intermetallic compound, and then we could get the galvanic current between the intermetallic and the Al matrix. The next problem is to prepare a pure intermetallic specimen.

As we know, it is not easy to produce a pure intermetallic specimen with a large area or volume, so an Al-8Fe-Ni alloy specimen that contains a huge amount of Al$_3$Fe intermetallic was used. Figure 5.13 shows the micro-structure of the Al-8Fe-Ni alloy. We find that the intermetallic is needle shaped.
In order to get the pure electrochemical performance of Al$_3$Fe intermetallic, the specimen must be treated to remove the influence coming from Al matrix. The method is as following:

1. **Specimen preparation:** Cut the specimen to $8 \times 9 \times 4$ mm$^3$ cube. A copper wire is welded on one face of the sample. The surface of specimen together with its copper wire is covered with lacomite, only a relatively large area is un-covered. Grind the un-covered surface with 320, 500, 1000, 4000 ground paper, and finally wash it with Milli-Q water.

2. **Electrochemical etching:** The solution used for electrochemical etching is 10 vol.% HCl, and the current density selected is 10 mA/cm$^2$ (Jiang and Wang, 1984). Pt is used as auxiliary electrode, and a Model 173 Potentiostat/Galvanostat is used to control current density. The specimen is normally etched for 2 hrs to get the deep etching result.
3. **Filling sample surface with EPOFIX:** After etching, Al matrix will be dissolved to a certain depth, the intermetallic should stand out of Al matrix. The specimen is carefully washed with Milli-Q water and dried in air. Then the specimen surface is filled with EPOFIX in vacuum conditions. In this case the air in the pores can be pumped out, this gives the best filling result. At the beginning, lacomite was used as a filling material, but it does not bond with Al-8Fe-Ni alloy very well. After polishing, almost all the lacomite was removed from investigated surface.

4. **Polishing:** When the EPOFIX had solidified after leaving in the air for 8 hrs, the specimen surface was ground carefully with 4000 ground paper until the intermetallic was exposed. There was then a final polish to 1 μm.

![Figure 5.14](image)

**Figure 5.14** The method of intermetallic specimen preparation. (a) original specimen, (b) after dissolving matrix, (c) filling with EPOFIX, (d) polishing to expose intermetallic surface.

The above steps are displayed in Figure 5.14. This method had been used by Lev (1962) when he measured the polarization curve of Fe₃C. The filling material he
used was varnish. He found that the holes left on the surface after dissolving were too small and varnish could not fill the gaps very well. Fortunately, the intermetallic in Al-8Fe-Ni alloy used in our experiment is large enough.

Before the electrochemical experiment, the area ratio of intermetallic on the specimen surface has to be determined. As the intermetallic is uniformly distributed on the sample surface, ten backscatter electron images were collected randomly for image analysis. The instrument used here is QUANTIMET 970, which is produced by Cambridge Instrument. The area ratio of intermetallic is about 17%, hence the effective specimen surface for each working electrode can be calculated.

Polarization curves for the Al₃Fe were acquired in 3 wt% NaCl solution at a scanning rate of 0.2 mV/S. From the polarization curve, we found that the corrosion potentials displayed in repeat curves changed a lot. Frequently they shifted more than 100 mV, that is from -800 to -700 mV (SCE). This indicates that the surface properties of the intermetallics are not stable. From the cathodic polarization part of the curve, we can find the cathodic current to be quite high.

Cyclic potentiodynamic polarization experiments were also performed on Al₃Fe intermetallic. In this case, although the corrosion potentials changed a lot when scanning in the positive direction, the potential was very stable when scanning in the negative direction. It was almost constant at -620 mV (SCE) (Figure 5.15). The reason for this is not very clear. Most probable is that there is some free Al in the intermetallics. When scanning in the potential positive direction, the free Al is oxidized first, so the corrosion potential is negative. When scanning the potential to negative direction, the free Al on the surface is dissolved already, and thus the electrode potential shown in scanning in the negative direction expresses correctly the intermetallic electrode potential.

Scanning in either direction shows a high cathodic current density. If this curve is overlapped with the polarization curve of 6061 Al alloy and supposing the anodic
area is equal to the cathodic area, we can find corrosion current density from the cross point of anodic polarization curve of 6061 Al and cathodic polarization curve of intermetallic. The current density is about 70 $\mu$A/cm$^2$.

5.3.2 The Influence of Relative Areas in MMCs

From the result above, we can directly read the galvanic corrosion current density for each component existing in MMCs with 6061 Al alloy from the polarization curves, but this is under the assumption that the areas of cathode and anode are equal. In the real situation, the anodic area is much more larger than the cathodic.
area. In conductive solutions, coupling will yield a corrosion potential determined by the following condition:

$$\sum I_a = \sum I_c$$

Where $I_a$ is the total anodic current and $I_c$ the total cathodic current at the particular potential. By taking a simplified system we can write

$$A_a i_a = A_c i_c$$

where $A_a$ and $A_c$ are the areas of anode and cathode respectively, and $i_a$ and $i_c$ are the corresponding anodic and cathodic current densities.

**Figure 5.16** Relative areas influence galvanic corrosion potential to the negative direction, so $i_c$ is larger than the original value, the $i_a$ is smaller than the original value.
Table 5.3 Cathodic current densities at different corrosion potential ($\mu$A/cm$^2$)

<table>
<thead>
<tr>
<th></th>
<th>Cathodic current density when $A_c = A_a$</th>
<th>Cathodic current density at Al corrosion potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCS-6 fibre</td>
<td>31</td>
<td>33</td>
</tr>
<tr>
<td>un-sized carbon fibre</td>
<td>70</td>
<td>80</td>
</tr>
<tr>
<td>FeAl$_3$</td>
<td>60</td>
<td>160</td>
</tr>
</tbody>
</table>

In the SiC reinforced Al MMCs, for example, the intermetallic particulate is very small, it is about 1 to 3 $\mu$m in diameter. The anodic area can be the whole matrix. As the total cathodic current equals to the total anodic current, the anodic current density is much lower than the cathodic current density. That means the corrosion potential will drop down to the negative direction (Figure 5.16, Figure 5.16). It is not easy to calculate the area fraction of the cathode, so the correct galvanic corrosion potential can not be determined. In the extreme situation, the galvanic corrosion potential will drop to the Al alloy corrosion potential.

Table 5.3 lists the cathodic current densities at different potentials for the materials that are used in the SiC/Al MMCs. For SCS-6 fibre and un-sized carbon fibre, the shift of galvanic corrosion potential does not influence cathodic current densities a lot. For the intermetallic, however, the cathodic current densities increase almost three times when the galvanic corrosion potential drops down to the Al corrosion potential. So in a real situation, the cathodic current density on an intermetallic particulate should be between 60 and 160 $\mu$A/cm$^2$, which is larger than the cathodic current density on un-sized carbon fibre and SCS-6 fibre. That means the most serious galvanic corrosion will happen
between intermetallic and Al matrix.

Figure 5.17 SEM micrograph for the SiCp/6061 Al MMC specimen which is anodic polarized at the potential of -650 mV in 3% NaCl solution open to air.

5.3.3 Potentiostatic Polarization

Anodic polarization of SiCp/6061 Al MMC was performed in neutral 3% NaCl solution. In the first instance, the SiCp/6061 Al MMC was anodically polarized at 0 mV (SCE) for 1 min and the morphology of the specimen was examined as shown in Figure 5.18. In previous results, we always found the corrosion was first observed around intermetallic particulates. When the anodic polarization potential applied to SiCp/6061 Al MMC is -650 mV, which is about 50 mV more positive than the corrosion potential, micro-galvanic corrosion can be found between Al matrix
Figure 5.18 SEM (top) and backscatter (bottom) morphology for the SiCp/6061 Al specimen which is anodic polarized at potential of 0 mV (SCE) for 1 min.

and intermetallic particulates. Figure 5.17 shows this phenomena. Gaps between SiC particulates and matrix can also be found after anodic polarization. Pits can
be observed on the surface of this specimen as shown in the micrograph of Figure 5.17. After the specimen is strongly anodic polarized, the pits seem not to be strictly correlated with the intermetallic particulates. Comparing the SEM and backscatter micrographs, we can find that intermetallic particulates may exist in the pits, but pitting may also have occurred at places where intermetallic particulates are absent. Significantly, many intermetallic particulates could be seen without corrosion around them.

![Figure 5.19](image)

**Figure 5.19** SEM micrograph for the specimen of 6061 Al alloy which is anodic polarized at -650 mV (SCE) in 3% NaCl solution open to air.

Anodic polarization is also performed on 6061 Al alloy. When the polarization potential applied on the specimen is 0 mV, pits can be observed on the specimen surface by inspection. The number of pits seems less than the pits on the SiC<sub>p</sub>/6061 Al MMC when the same polarization condition is used. Figure 5.19 shows the micrographs of 6061 Al alloy, which is anodic polarized at -650 mV (SCE). There
is no strong evidence that the pits are initiated from the intermetallic particulates, but galvanic corrosion can be found around some of intermetallics, even if it does not happen around all the intermetallics.
Chapter 6 Discussions

The experimental results are shown and discussed in chapter 4 and 5. Some questions arose from this project after finishing the experimental works. They will be discussed in the following sections of this chapter.

6.1 THE BREAKDOWN OF THE PASSIVE FILM

As mentioned in literature survey, some special positions are susceptible to passive film breakdown. These positions include intermetallic particulates, nonmetallic inclusions, grain boundaries, local scratches or abrasions, differential stain, and dislocations etc. In this part of work, it is shown that the dominate factors that can induce passive film breakdown are intermetallic particulates and reinforcements in MMCs.

Surface analysis experiments have shows that intermetallic particulates can form micro-galvanic cells with the matrix Al alloy. In aerated NaCl solution the cathodic reaction, \(2O_2 + 2H_2O + 4e = 4OH^-\), occurs at intermetallic surfaces. The reaction product is hydroxide ion, which can increase the local pH value. Ion decoration experiments show that when the concentration of \(Mg^{2+}\) comes up to 0.01 M, \(Mg(OH)_2\) can be found at an intermetallic particulate. As the solubility product of \(Mg(OH)_2\) \((K_{sp} = [Mg^{2+}]\cdot[OH^-]^2)\) is \(1.8 \times 10^{-11}\), the pH value must surpass 10.1 to result in the formation of \(Mg(OH)_2\). We will now look at the influence of such high pH value on the corrosion of the aluminium matrix.

Deltombe et al (1966) have drawn a series of curves (Figure 6.1) expressing the influence of pH on the solubility of the five forms of alumina (Table 6.1) for which they knew the free enthalpies of formation. The physical and chemical properties of alumina depend to a large extend on the temperature reached during its preparation. The ordinary variety is corundum or \(\alpha\)-alumina, crystallizing in the
Figure 6.1 Influence of pH on the solubility of $\text{Al}_2\text{O}_3$ and its hydrates, at 25 °C.

rhombohedral system. As we can find from those curves, the solubilities of all forms of $\text{Al}_2\text{O}_3$ are increased more than two orders of magnitude when the pH value increases from 7 to 10.1.

<table>
<thead>
<tr>
<th>Hydrargillite</th>
<th>$\text{Al}_2\text{O}_3\cdot3\text{H}_2\text{O}$</th>
<th>Monocl.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bayerite</td>
<td>$\text{Al}_2\text{O}_3\cdot3\text{H}_2\text{O}$</td>
<td>Monocl.</td>
</tr>
<tr>
<td>Böhmite</td>
<td>$\gamma\text{-Al}_2\text{O}_3\cdot\text{H}_2\text{O}$</td>
<td>Tern.</td>
</tr>
<tr>
<td>Corundum</td>
<td>$\alpha\text{-Al}_2\text{O}_3$</td>
<td>Tern.</td>
</tr>
<tr>
<td>Amorphous hydroxide</td>
<td>$\text{Al(OH)}_3$</td>
<td>Amorphous</td>
</tr>
</tbody>
</table>
As a result of the micro-galvanic cell between the intermetallic particulates and the Al matrix, the pH value will increase in the immediately surrounding region (Figure 6.2). The influence of this pH change will depend on the nature of the pre-existing passive film. Hunter and Fowle have stated that only amorphous oxide was found at low temperatures, or at intermediate temperatures for short times. The specimens used in this project were normally kept in dry air for a few weeks, so the oxide film would have increased in stability but will still probably lie between amorphous hydroxide and Böhmite. The solubility of these aluminium oxides is very high at pH value of 10 as shown in Figure 6.1, and thus as the pH increases to this value the passive film may be expected to dissolve more rapidly. When the original oxide film is destroyed, the new oxidized aluminium will form amorphous Al(OH)$_3$ because of the high pH value. This film no longer has the ability to protect against Al corrosion, and there is thus an auto-catalytic effect on the galvanic corrosion between the intermetallic particulates and the surrounding Al matrix. This would explain the strong localization of the matrix corrosion at the intermetallic particle. This auto-catalytic influence of the pH change caused by the intermetallics disappears when, as a result of strong anodic polarization, the cathodic reaction on the intermetallic particle is quenched (section 5.3.3).

If experimental specimens are stored for a very long time or if they are treated by anodization or high temperature, the stability of oxide will be increased and the effect of local pH changes may not be observed. The solubility of hydragillite is about 10000 times less than amorphous hydroxide at pH 10 as shown in Figure 6.1.

In the course of this work, a paper was published which provide in an interesting way that intermetallic particles remain active in corrosion cells down to much smaller size than can be observed in the SAM. Shimizu et al (1993) showed that ultramicrotomed slices containing an intermetallic particle undergo corrosion when immersed in the aqueous phase of the cutting machine. The subsequent TEM analysis showed the presence of hydrated aluminas surrounding Al$_3$Fe. This had occurred and caused deposit in the manner described in this present work.
Chapter 6  Discussions

There is limited $O_2$ dissolved in solution. As mentioned by West (1986), pure water saturated with air ($P_{O_2} = 0.2$ atm) contains some 40 ppm oxygen at 20 °C. Thus
the \( \text{O}_2 \) contained in solution near the cathode region is quickly consumed and the corrosion rate becomes controlled by oxygen diffusion. From the potentiodynamic polarization curve of 6061 Al alloy and the cyclic polarization curve for Al\(_2\)Fe intermetallic (Figure 5.15), we can find that the corrosion potential of the galvanic cell between Al and intermetallic is located at the mixed (Tafel and diffusion) control region. If we consider the factor that the passive film is less stable after the initiation of micro-galvanic corrosion, which is discussed in last paragraph, the corrosion potential of Al will be likely to move to the electrode potential of pure Al, that is lower than -800 mV (SCE). In this case, the corrosion potential of the galvanic cell between the Al matrix and the intermetallic would move to negative direction as well, which will locate at the region of \( \text{O}_2 \) diffusion control region at the intermetallic electrode. The changing electrochemical situation is related to the diagram illustrating corrosion in Figure 6.2. As can be seen the galvanic corrosion current will increase as a result of this loss of protection in the region of the intermetallic and become close to the range of current densities calculated from the models used in section 4.3.6.

In addition to intermetallic particulates, the SiC particulates in Si\(_c\)/6061 Al MMC are also a factor to induce the passive film breakdown. The surface analysis and potentiodynamic polarization experiments show that there is no galvanic effect between silicon carbide and Al alloy, but cracks can be found at the phase boundary between SiC particulates and Al matrix when the Si\(_c\)/6061 Al is polarized by the potentiostatic method or after long time exposure to NaCl solution. The most likely corrosion problem related to SiC particles is crevice corrosion. Since these crevices are angular, following the shape of the SiC particle and do not present in the shape of a ring which is characteristic of the micro-galvanic cells. The reason for this crevice corrosion is probably the difficulty of sustaining a protective film across the phase boundary; as such the phenomenon is classic in its cause. There are also some small sites of ‘half-halo’ attack at the SiC. Small impurity particles present at the interface are probably the main factor.

One piece of evidence shows the susceptibility to breakdown of the passive film at
the boundary of SiC particulates and the Al matrix. When preparing SiC\textsubscript{p}/6061 Al MMC specimen, we normally polish the specimen about half minute by using OP-S suspension. When using OP-S, chemical attack forms a brittle reaction layer on the specimen surface which is easily removed by the mechanical polishing action. Once the specimen is polished longer than 3 minutes, the corrosion will occur at the boundary between SiC particulates and Al matrix as is displayed in Figure 6.3. The OP-S suspension has a high concentration of alkali, the pH value is about 9.5. At this pH chemical attack occurs around the whole specimen surface, but the boundary region is difficult to re-passivate and deeper attack occurs at this location.

As discussed above the local corrosion is either related with the intermetallic particulates or with SiC particulate reinforcement. Different mechanisms of localised corrosion are related to these two particles, the local corrosion correlated with the intermetallic particulates is much more serious compared with the corrosion related to the SiC particulates. It is not clear whether the local attack
can develop to a pit or will be repassivated.

For the SiC fibre reinforced Al MMC, the reinforced fibre can also form galvanic cell with Al matrix due to the carbon core and carbon coating. This galvanic cell will exist during the whole period that the material is exposed to the aqueous environments, or in moist air. Fibres will be de-bonded with the matrix as a result of corrosion. This material will finally loose its mechanical properties for which it is designed.

### 6.2 THE CONSIDERATION OF COMPOSITE DESIGN

#### 6.2.1 SiC/6061 Al MMC

Silicon carbide particulates can induce the crevice corrosion in SiC/6061 Al MMC, but it gives way to micro-galvanic corrosion correlated to the intermetallic particulates in MMCs. So SiC particulates are not the dominant factor inducing the local attack. Many researchers have found that there are more intermetallic particulates in MMCs than in the plain alloy, one method for increasing corrosion resistance of MMC is to reduce the number of intermetallic particulates. In our research, we found that the Fe containing intermetallic particulates can form a galvanic cell with the matrix in SiC/6061 Al MMC. If these particulates contain enough Cr the property of the intermetallic is changed, it does not behave as cathode any more. This may be understood by reference to Figure 5.15 in which the intermetallic is shown to be activated by the cathodic potential. This is thought to arise from reduction of the passivating oxide on the particle. In the case of Cr-containing particulates, it is unlikely that they would be activated in the same way by the cathodic potential because of the stability of Cr oxide. This kind of intermetallic is found in SiC/6061 Al MMC. As the fabrication procedure is not published by the manufacturers, it is difficult to say how to change the Fe
containing intermetallic to both Fe and Cr containing intermetallics. It is suggested that when fabricating MMCs for the purpose of use in corrosive environments, the secondary phases in the matrix should be designed to have low cathodic activity.

6.2.2 SiC/6061 Al MMC

The local attack in SiC/6061 Al MMC is directly related to the SiC fibre reinforcement. The CVD-SiC fibre in the MMC examined in these studies utilizes a carbon substrate, coated with SiC. It is well known that graphite has a low over-potential for O₂ reduction. From the results of the XPS image analysis, the C core is mainly composed of graphite. It is not surprising therefore that the carbon core shows a cathodic effect when it is exposed to the electrolyte. SiC has a very poor conductivity, but the electrochemical activity resulting from this will be influence by the layer of SiC as it separating the C core and Al matrix, the thickness of SiC between the C core and Al matrix is only about 50 μm. Unfortunately, it cannot insulate the C core from the Al matrix and electrons can pass through this layer as a result of the galvanic corrosion.

A, SiC fibre with a W core is also popular for the use in MMCs. The same corrosion problem may happen on the Al MMCs with this form of reinforcement due to the reasons outlined above.

In production of the fibre, at the end of SiC deposition, the fibre surface is covered with a carbonaceous coating by varying the processing conditions and composition of the reactant gases. Carbon coating results in a significant increase in fibre strength due to the healing of surface flaws (Cornié et al., 1981). From the viewpoint of corrosion, this coating has a high cathodic activity even thought the carbon coating is finally overcoated with SiC.

The fibre used in continuous SiC reinforced Al MMC is normally fabricated by a chemical vapour deposition method. In this technique the substrate acting as core
should have reasonable electric conductivity, but because of this it can form a
galvanic cell with the matrix alloy if it does not have the same electrode potential
as the matrix alloy, or if it cannot be passivated. Another commercial SiC-based
fibre is called "Nicalon", which is made from a spun polymer precursor (Parvizi-
Majidi, 1993). Nicalon fibres have a non-stoichiometric composition consisting of
SiC, SiO$_2$, and free C. The presence of SiO$_2$ accounts for the lower Young's
modulus of Nicalon compared to the CVD-derived SiC fibres. The small amount
of free C may have cathodic effect, but it should be much better than the pure C
core in CVD-derived SiC fibres. Research is still being undertaken to develop new
fabrication methods for SiC fibres and some of these products, like Nicalon, may
have improved galvanic performance.

6.3 PROTECTIVE CONSIDERATIONS

MMC materials are normally more susceptible to corrosion attack than the matrix
alloy. Protection methods would improve the acceptability of MMCs when they are
to be used in corrosive environments. To get a protective effect, efforts can be
directed to control the anodic dissolution, cathodic reaction, or both of them.
Protection by coatings, through anodizing or chemical conversion coatings possibly
with an organic topcoat, is readily feasible. In appropriate circumstances, corrosion
inhibitors can be used in a relatively closed system.

There are two reasons to make me consider that the approach to reduce the
cathodic reaction rate may be better than to decrease the anodic reaction. Firstly,
the corrosion rate of MMC in neutral solution is controlled by oxygen reduction on
cathodic regions. Either decreasing the concentration of O$_2$ dissolved in the
solution or increasing the overpotential of cathode for O$_2$ reduction will reduce the
corrosion rate. Secondly, due to the existence of reinforcement phases in MMCs,
crevice corrosion maybe present even if a protective surface film is formed on the
MMC surface. For example, a few anodization treatments or chemical passivation methods were investigated by Mansfeld et al. (1986, 1987, 1988, 1989, and 1990). Corrosion resistance of MMCs was significantly increased, but crevice corrosion caused by the presence of the SiC particulate reduced the corrosion resistance.

Organic coatings provide corrosion protection by acting as a barrier layer between the substrate material and the environment. They have the potential to be used for corrosion protection of MMCs, especially for unidirectional fibre reinforced MMCs on the surface where the fibre is exposed. The main problem to be overcome is the adhesion. The differences in surface properties between metal and reinforcement could drastically affect the distribution and adherence of protective coatings. Additionally, the suitability of using coatings for corrosion protection of metal matrix composites depends on the effects of the coating on the mechanical, physical, and dimensional requirements of the application. An attempt at coating was made by Lin et al. (1992). In their work, epoxy resin (hysol G7-4102, Dexter Corp.) was applied to Al 6061, Al/Gr, Al/SiC, Al-Li 2091-T6 and MgAZ31B. This protective coating provides excellent corrosion resistance, but when the coating is damaged, rapid corrosion and coating delamination occurred at the damaged area.

6.4 GALVANIC CURRENT IN MICRO-CORROSION CELLS

Two different diffusion models were used to estimate the cathodic current density on the intermetallic particle surface. The spherical model is closer to the real situation than the plane sheet model for intermetallic particle. The situation for the carbon coating and the carbon core of the SiC fibre is more complicated and if the spherical diffusion model is used, the calculation error will be bigger than the calculation for the intermetallic particle.

In addition to the approximation inherent in the use of the diffusion equation, there
are two factors that may impair the accuracy of cathodic current densities estimated by ion decoration. The first one is the estimation of critical concentration for magnesium deposition, the second one is the estimation of diffusion layer thickness of hydroxide ions.

The concentrations of MgCl$_2$ used in the ion decoration experiment were 1 M, 0.1 M, 0.01 M, 0.001 M, and 0.0001 M. For example, we knew that a magnesium deposit was found on the carbon core position after the SiC$_x$/6061 Al MMC specimen was immersed in the 0.1 M MgCl$_2$ solution. So 0.1 M was accepted as critical concentration for the magnesium deposition. Actually, the critical concentration is between 0.1 M and 0.01 M. If it is near to 0.01 M, the cathodic current density is three times larger than the estimated result. The situation is the same for the intermetallic particle and carbon coating.

The second factor is the diffusion distance. The value used does not have a large influence on the calculated result when the spherical diffusion model is used, but the calculated result depends very strongly on the diffusion distance if the plane sheet diffusion model is used. It is difficult to measure the value of the diffusion distance of hydroxide directly. For the intermetallic particle, we assumed that the diffusion distance was twice of the radius of the intermetallic particle. In the real situation, the diffusion distance of OH$^-$ that was produced by the oxygen reduction may be much larger than this. If it is like that, the result of cathodic current density that is calculated by using plane sheet diffusion model will be smaller, but a little changed by calculation on the basis of the spherical diffusion model.

To confirm the estimates from the ion decoration technique, an electrochemical technique was also used to measure the cathodic current density, and to further assess the corrosion rate. The values obtained were smaller than the estimated values. The cathodic current densities measured by the electrochemical method are more direct, and do not have the approximations made in the ion decoration method, so the cathodic current densities measured by electrochemical method should be more correct than the value estimated by the surface analysis technique.
However, the shape of electrodes in the electrochemical experiment and in the ion decoration experiment were not same, so the different diffusion models were involved in the processes. The cathode electrode and ion diffusion path is closer to the real situation in the ion decoration technique. Thus it is difficult to say which method is more accurate to estimate cathodic current density in composite materials, but it would be wise to use the large values estimated by ion decoration until better measurement can be made.

6.5 THE RESISTANCE OF SiC

In the galvanic circuit made by carbon core and Al matrix, a thick layer of SiC can produce an ohmic (IR) drop between cathode and anode. The IR drop is equal to $I_{galv} \cdot R$, where $R$ is the resistance of the galvanic circuit. $I_{galv}$ decreases as the IR drop increases. The resistance, $R$, of SiC can be calculated by the following equation:

$$ R = \frac{\rho}{2\pi l} \ln \frac{D}{d} $$

where $\rho$ is the resistivity of SiC, $l$ is the fibre length, $D$ and $d$ are the outer and inner diameters of SiC respectively. From the CRC Handbook of Chemistry and Physics, the electrical resistivity of SiC at room temperature is 107-200 ohm-cm. The outer and inner diameters of SiC are 141 and 38.6 µm respectively, the dimension of the specimen in the axial direction was about 0.5 cm, so the length of the fibre is about this value. If we accept the electrical resistance of SiC as 200 ohm·cm, the resistance between carbon core and Al matrix caused by the SiC should be 82.5 ohm. The ohmic drop, $I_{drop}$, can be calculated by the following equation:
\[ \text{IR}_{\text{drop}} = i \cdot A \cdot R \]

where \( i \) is the cathodic current density on carbon core, \( A \) is the area of carbon core and \( R \) is the resistance of SiC. \( i \cdot A \) is equal to the total current passing through the galvanic cell. The cathodic current density on the carbon core can be estimated from the cathodic polarization curve of the carbon fibre. The value of ohmic drop can be calculated by Eq 6.2, it is \( 6.8 \times 10^{-5} \) mV. So the ohmic drop which is caused by SiC is very small, it can be neglected.

### 6.6 EVALUATION OF THE METHODS

#### 6.6.1 Surface Analysis Technique

The Auger analysis technique is successfully used in this project to observe the initial stage of local corrosion caused by micro-galvanic corrosion cell. This technique has many advantages: It can tell us what kind of particles can induce galvanic corrosion and the composition of corrosion products, so that the cathode and anode area can be mapped out; Due to the high spatial resolution, particles of only one micrometer in size can be investigated; The initial corrosion rate can also be estimated by using an ion decoration method if some parameters, such as diffusion distance \( \delta \), can be determined by other techniques.

There are disadvantages of Auger analysis. Many Auger peaks are too broad and influence the observation of the chemical state. The Auger electron peaks are small and often superimposed on a sloping background in the direct spectrum, so it is also not easy for the quantitative analysis. XPS is good in energy resolution and the quantitative technique is more mature than AES, but the spatial resolution is poor. Although the high spatial resolution XPS instrument is available now, it is still not very good for the investigation of local corrosion with a scale of a few
6.6.2 Scatter Diagram Analysis

The Scatter Diagram is a very useful tool for the study of complex surfaces. It is successfully used in this project for the identification of the phases and deposition. It could be a very useful method for quantitative analysis of surface images. An example of the use of such diagrams is as follows:

If an Al specimen is heated at 300 °C, the specimen surface will be covered with $\text{Al}_2\text{O}_3$. As described in chapter 4, the chemical shift of aluminium can be found when the high constant retard ratio is used. By using the SAM technique, the aluminium ion and oxygen maps can be collected simultaneously. Scatter diagram analysis can be applied to those two maps, in which the maps were topographically corrected. Then the oxygen/aluminium ratio can be obtained from the slope of the centre of the cluster spot. This ratio corresponds to the stoichiometry $\text{Al}_2\text{O}_3$.

The same procedure can be used on the specimen before and after corrosion around the position that is sensitive to the local corrosion, such as intermetallic particle, and then the composition of aluminium oxide film and corrosion products can be obtained. This method is displayed in Figure 6.4.

In a practical situation, there are several factors which restrict the use of this method. The intensities of images were normalized to 255 in our program, this normalization can influence the accuracy of the quantitative result. If this method is to be used, the real counts of each image must be plotted, then the slope in Scatter Diagram can be used to calculate the ratio of oxygen/aluminium. The problem is that the computer linked with MA500 has very small memories, it cannot process a large amount of data. It is not compatible with the IBM PC, so the data cannot be transferred. This problem can be overcome now in the modern Auger Microscope, since the computer based data systems have developed very
Figure 6.4  Schematic diagram shows the identification of the composition of aluminium oxide film and corrosion products by using Scatter Diagram.

quickly in recent years.
Chapter 7 Conclusions

Through the experimental results, the following points can be concluded.

1. Surface analysis techniques are advanced methods to investigated the initiation of corrosion. Among these techniques, Scanning Auger Microscopy has a distinctive advantage in study of localised corrosion. As SAM is combined with simultaneously EDX analysis, the elemental distribution information both from surface and bulk can be collected together. This is very useful for investigating the micro-galvanic corrosion related to the secondary phases.

2. Certain kind of intermetallic particulates existing in Al alloy and Al matrix composites can induce micro-galvanic corrosion. These intermetallics mainly contains Fe, Ti or Cu. If some Cr exists in the Fe-containing intermetallic particulate, this intermetallic will be passivated and there will be little or no galvanic reaction occurring. SiC particulates do not show a strong relationship with micro-galvanic corrosion.

3. The intermetallics normally act as cathode. The main cathodic reaction occurring on the surface of intermetallic particulate in neutral NaCl solution is the reduction of oxygen, which is dissolved in the solution. That is:

$$O_2 + 2H_2O + 4e = 4OH^-$$

The cathodic reaction can be recognized by using surface analysis techniques if a certain cation is added in the solution. In this project Mg$^{2+}$ is used to decorate the cathodic regions.

4. The Al matrix surrounding intermetallic particulates acts as anode, the corrosion products being recognisable by the greater oxygen content of the compound(s) formed when compared to that of the surrounding passive film. The generation of OH$^-$ at the cathode may give an auto-catalytic effect.
5. SiC particles existing in SiC$_p$/6061 Al MMC are not involved in micro-galvanic corrosion. However, crevice corrosion can be observed at the SiC/Al interface, probably arising from the poor quality of the oxide film at the phase boundary. The corrosion problem caused by SiC particles is not as serious as that associated with the intermetallics.

6. Unlike SiC particles, SiC fibre can induce galvanic corrosion of Al matrix. This is due to the carbon core and the carbon coating present in the SiC fibre. Both the carbon core and the carbon coating play a cathode role in the galvanic cell. The thick SiC layer between the carbon core and Al matrix does not obstruct the passage of electrons.

7. The current flow in the galvanic cell can either be identified by surface analysis techniques or by electrochemical experiment performed on the individual components of the galvanic cell.

8. An attempt to estimate the galvanic corrosion rate was made both by surface analysis techniques, i.e., by magnesium ion decoration, and by electrochemical experimental data. Both methods have their advantages and disadvantages.
Appendix: Corrosion of SiC<sub>p</sub>/2124 Al MMC and Its Matrix Alloy

Aluminium alloys, because of their low density and excellent strength, toughness, and resistance to corrosion, find important applications. Aluminium-copper alloys are widely used for structural applications in the aircraft industry and in general engineering when light weight combined with strength is required. In this section, concentration is focused on the corrosion properties of 2124 Al alloy and 15% SiC<sub>p</sub>/2124 Al MMC. These materials, which were fabricated by a powder metallurgy method, were provided by BP. The composition of commercial 2124 Al alloy is listed in Table A.1. The specimens for experiments were prepared as for SiC<sub>p</sub>/6061 Al MMC. The same concentration of NaCl and MgCl<sub>2</sub> solutions were used in this part of experiments as in the early work.

<table>
<thead>
<tr>
<th>Table A.1 The composition of 2124 Al alloy</th>
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<tr>
<td>(Metals Handbook, Disk Edition)</td>
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<tr>
<td>Cu</td>
</tr>
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<td>4.4</td>
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The microstructure of 2124 Al alloy and SiC<sub>p</sub>/2124 Al MMC are shown in Figure A.1. Comparing with the SiC<sub>p</sub>/6061 Al MMC and its matrix alloy, there are a lot more intermetallic particulates in this specimen. The backscatter micrograph (Figure A.2) can distinguish SiC and intermetallic particulates in SiC<sub>p</sub>/2124 Al MMC, the intermetallics being brighter than other places due to the
greater concentration of much more heavy elements contained in these particles. EDX analysis shows that the intermetallic particulates mainly contain Cu and Al. From a knowledge of the possible phases in 2124 Al alloy, the intermetallic is
Figure A.2 The backscatter micrograph of 15% SiC/2124 Al MMC.

Figure A.3 EDX spectrum on the point of intermetallic particulate in SiC/2124 Al MMC.

probably Cu$_2$Al.
A2. LONG TERM EXPOSURE EXPERIMENT

15% SiC_p/2124 Al MMC and 2124 Al alloy were exposed in 3% NaCl solution at pH value of 7.2 for 191 hours. Both SiC_p/2124 Al MMC and its matrix alloy suffered very serious corrosion attack as compared with SiC_p/6061 Al MMC and 6061 Al alloy. After exposure, a lot of white corrosion products deposited on the specimen surface, and were even present in the NaCl solution. The composite materials suffered more serious corrosion. The corrosion products on the composite surface were difficult to remove, so the SiC_p/2124 Al MMC specimen was ultrasonically cleaned in Milli-Q water for 1 min. Figure A.4 shows the micrographs of 2124 Al alloy and SiC_p/2124 Al MMC after exposure in 3% NaCl solution at pH value of 7.2 for 191 hr. A very thick corrosion products layer exists on the 2124 Al alloy surface as a lot of cracks can be seen on the micrograph. For the SiC_p/2124 Al MMC specimen, the corrosion products on the surface were removed by ultrasonic cleaning in some areas, but some areas still remained covered with thick corrosion products. The significant difference between 2124 Al composite or alloy and 6061 Al composite and corresponding alloy is that there are no distinct pits on 2124 Al composite and alloy, i.e., 2124 Al MMC and its matrix alloy experienced more serious uniform corrosion.

A3. ELECTROCHEMICAL EXPERIMENTS

The conditions of electrochemical experiments used are the same as before, which were described in Chapter 5. Figure A.5 are the potentiodynamic polarization curves for SiC_p/2124 Al MMC and 2124 Al alloy. From these curves we found that the corrosion potentials of these two materials are nearly the same. The corrosion potential of 2124 Al alloy is -688 mV, and SiC_p/2124 Al MMC is -695 mV. These
Appendix: Corrosion of SiC/2124 Al MMC and its matrix alloy

Figure A.4 Micrographs of 2124 Al alloy (top) and SiC/2124 Al MMC (bottom) after exposure in 3% NaCl solution at pH value of 7.2 for 191 hr.

corrosion potentials are slightly more positive than the SiC/6061 Al MMC and its matrix alloy. That is due to the greater copper content in 2124 Al alloy. The SiC/2124 Al MMC can support less cathodic current density than 2124 Al alloy.
If the area ratio correction is made, the cathodic current density is still a little smaller. The anodic current density of SiC/2124 Al MMC at low anodic polarization potential is smaller than 2124 Al alloy, but it becomes larger at higher anodic polarisation part. That means more pits are developed on the MMC material surface.

Comparing the potentiodynamic polarization curves of 6061 Al and 2124 Al alloy (Figure A.6), we can find that the cathodic current densities of these two alloys have some difference. The 2124 Al alloy can suffer larger cathodic current density than 6061 Al alloy. These phenomena may relate to a more conductive surface on 2124 Al alloy. Generally, aluminium is covered with a highly protective oxide film of alumina, Al₂O₃. This is an n-type semiconductor containing anion defects, and its conductivity is extremely low. As the 2124 Al alloy contains 4.4% Cu, the
Appendix: Corrosion of SiC/2124 Al MMC and its matrix alloy

Figure A.6 The comparison of potentiodynamic polarization curve of 1: 6061 Al and 2: 2124 Al alloy.

presence of copper will lower the resistance of the film considerably.

Potentiostatic polarization was performed on SiC/2124 Al MMC and its matrix alloy. The numbers of pits found on these two materials' surfaces after anodic polarization are not as much as that can be found on SiC/6061-Al MMC and corresponding 6061 Al alloy. Figure A.7 shows the morphology of SiC/2124 Al MMC after anodic polarization at -650 mV. We can find that some parts on the specimen surface are covered with thick corrosion products. This corrosion product is non-conductive, so the effects due to electrostatic charging can be found from the image. Some small pits also were present (Figure A.8). These pits are not strongly correlated with intermetallic particulates due to the cathodic reaction occurring on a separated electrode. Micro-galvanic corrosion still can be found at intermetallic particulates positions as comparing with the corresponding backscatter image. A dark halo exists around intermetallics. A similar situation can be found on 2124 Al
Appendix: Corrosion of SiC<sub>p</sub>/2124 Al MMC and its matrix alloy

Figure A.7  SEM image of SiC<sub>p</sub>/2124 Al MMC after anodic polarization at -650 mV.

alloy, which is shown in Figure A.9.

A4. SUMMARY

From the long term exposure experiment, we can find that SiC<sub>p</sub>/2124 Al MMC and its matrix alloy normally suffer less pit corrosion as comparing with SiC<sub>p</sub>/6061 Al MMC and its matrix alloy. The general corrosion problem is very serious, that is due to the less protective surface film which was formed on the 2124 Al surface. This is confirmed from the cathodic polarization curves.
Figure A.8 Top: the pits existing on SiC$_p$/2124 Al MMC specimen surface after anodic polarization at -650 mV, bottom: backscatter image of same area.
Figure A.9 The micrograph of 2124 Al alloy after anodic polarization at -650 mV.
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