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Electrochemical Studies on Localised Aluminium Corrosion and Its inhibition – Novel Approaches to Old Problems

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A thesis submitted to the Nanyang Technological University in
fulfillment of the requirement for the degree of
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Summary

This thesis mainly concerns the development and application of a novel electrochemical method, based on the combined use of the wire beam electrode (WBE) and scanning reference electrode technique (SRET), for the study of localised corrosion of aluminium (AA1100) and aluminium alloy (AA2024-T3) and its inhibition.

The WBE and the SRET have been applied in a novel combination to measure, for the first time, electrochemical parameters simultaneously from both the metallic and electrolytic phases of a corroding metal surface. In general, the WBE and SRET have been found to be useful for understanding the formation, stable propagation and the electrochemical behaviour of localised corrosion, and also its dependence on externally controllable variables such as solution pH, corrosion inhibitors and surface coatings. In particular, the WBE appeared to be able to reveal the corrosion patterns of all of the cases being investigated. A new concept namely localised corrosion intensity index (LCII) has been proposed, based on WBE data, to quantify the degree of localised corrosion.

The WBE and SRET have been applied to study the corrosion processes of AA1100 in various corrosive environments. It was found that corrosion of AA1100 was general at the very beginning of exposure to a corrosive environment, and became localised at the later stages of exposure. Corrosion became more serious with the presence of cupric ions in sodium chloride solution. Localised corrosion formation on AA1100 was found to be associated with the disappearance of minor anodes, leading to high anodic dissolution currents concentrating on a few remaining anodes.

The WBE and SRET have also been applied to the study of AA2024-T3. It was

found that in sodium chloride solution, AA2024-T3 generally underwent localised corrosion. The WBE revealed a clear corrosion formation period and a stable propagation period taking place on AA2024-T3 during its exposure to sodium chloride solution. A possible mechanism for explaining the aluminium matrix dissolution of AA2024-Ts has been proposed based on the synergetic process of dealloying, cathodic corrosion, and crevice corrosion.

The inhibition effects and mechanisms of corrosion inhibitors have been studied using the WBE and SRET in conjunction with other electrochemical methods. Inhibitors were studied by introducing them into corrosive media either at the beginning of corrosion exposure or at the later stages of corrosion exposure. The WBE maps showed that potassium dichromate and cerium chloride were anodic inhibitors, while lanthanum chloride was a cathodic inhibitor. The mechanism by which cerium chloride inhibits AA2024-T3 localised corrosion was found to be the formation of cerium rich passive film, especially insoluble cerium hydroxide/oxide around the dealloying S phase particles and active cathodic particles. It was found that with the presence of potassium dichromate or cerium chloride in sodium chloride solution, the corrosion pattern generally changed from localised corrosion to general corrosion. The efficiency of various inhibitors in protecting AA2024-T3 from localised corrosion was also evaluated using the corrosion current densities measured by WBE.

List of Symbol and Abbreviations

Symbol	Meaning
b_{ka}	Tafel slope for anodic polarisation of wire k in a WBE
b_{kc}	Tafel slope for cathodic polarisation of wire k in a WBE
CCCs	Chromate conversion coatings
CR	Corrosion rate
CR_0	Corrosion rate in sodium chloride solution
CR_{inhi}	Corrosion rate in sodium chloride solution with inhibitors
i_0	Corrosion current density obtained without the presence of inhibitor
i_{inhi}	Corrosion current density obtained with the presence of inhibitor
i_{corr}	Corrosion current density
i_{max}	Maximum anodic current density obtained from WBE measurement
i_{tot}	Total anodic current density obtained from WBE measurement
IE	Inhibition efficiency of inhibitors
E	Electrical potential
E_{corr}	Corrosion potential or open circuit potential
E_k	Corrosion potential of wire k in a WBE
E_{ka}	Equilibrium potential of the anodic reaction of wire k in a WBE
E_{kc}	Equilibrium potential of the cathodic reaction of wire k in a WBE
E_{np}	Pitting nucleation potential
E_{pp}	Protection potential
E_{pit}	Pitting potential
E_{sys}	Overall system potential of a WBE
EW	Equivalent weight
$1/f$	Reciprocal frequency of electrochemical noise
I_{gk}	Galvanic corrosion current of wire k in a WBE
I_k	Corrosion current of wire k in a WBE
I_{ka}	Anodic reaction current of wire k in a WBE
I_{kc}	Cathodic reaction current of wire k in a WBE

i_n	Anodic current density obtained of an individual wire in a WBE
κ	Solution conductivity
L	Length
LI	Localisation index
mA	Milliampere
mV	Millivolt
N_a	Number of anodes from WBE measurement
R_n	Electrochemical noise resistance
R_p	Polarisation resistance
ρ	Mass density
SCE	Saturated Calomel Electrode
SHE	Standard Hydrogen Electrode
AFM	Atomic Force Microscopy
AES	Auger Electron Spectroscopy
EDS	Energy Dispersive X-ray Spectroscopy
EIS	Electrochemical impedance spectroscopy
ENA	Electrochemical Noise Analysis
SEM	Scanning Electron Microscope
SRET	Scanning Reference Electrode Technique
SVET	Scanning Vibrating Electrode Technique
WBE	Wire Beam Electrode
XPS	X-ray Photoelectron Spectroscopy

List of Publications

(i) Journal Papers

Tan, Y. J.; Aung, N. N. and Liu, T. 'Novel Experiments Using the Wire Beam Electrode Method: (I) Studying Electrochemical Noise Signatures from Localised Corrosion Processes', *Corros. Sci.*, Vol. 48, 2006, pp 23-38

Aung, N. N.; Tan, Y. J. and Liu, T. 'Novel Experiments Using the Wire Beam Electrode Method: (II) Determining the effects of Ions Movement on Electrochemical Corrosion Processes', *Corros. Sci.*, Vol. 48, 2006, pp 39-52

Tan, Y. J.; Liu, T and Aung, N. N., 'Novel Corrosion Experiments Using the Wire Beam Electrode: (III) Measuring Electrochemical Corrosion Parameters from Both the Metallic and Electrolytic Phases', *Corros. Sci.*, Vol. 48, 2006, pp 53-66

Liu, T; Tan, Y. J.; Bernice Lin, Z. M. and Aung, N. N., 'Novel Corrosion Experiments Using the Wire Beam Electrode: (IV) Studying Localised Anodic Dissolution of Aluminium' *Corros. Sci.*, Vol. 48, 2006, pp 67-78

(ii) Conference Papers

Liu, T and Tan, Y. J. (2002), 'Mapping corrosion current over aluminum and mild steel surfaces using the scanning reference electrode technique', '*1st International Conference on Materials Processing for Properties and Performance*', Eds., Hhor, K. A.; Zhang, S. Y.; Hing, P. and Boey, F. Institute of Materials (EAST ASIA), pp 477-487

Tan, Y. J.; Liu, T. and Aung, N. N. (2004), 'Localized Corrosion and Inhibition Studies Using the Wire Beam Electrode in Conjunction with the Electrochemical Noise Analysis and the Scanning Reference Electrode Technique', *Corrosion 2004*, NACE, Houston, Texas

CHAPTER 1

Introduction

Aluminium exhibits excellent resistance to general corrosion, which is usually attributed to the formation of an inert and protective oxide film on its surface. However when exposed to an environment containing aggressive ions, aluminium and its alloys often suffer from localised corrosion attack. Localised corrosion of aluminium is a major concern in many industries such as the aircraft manufacturing and ship building sectors.

Inhibition is a technique that has been used for preventing aluminium corrosion for many years. Various corrosion inhibitors and pigments, and various application techniques have been developed for the inhibition of aluminium corrosion. For instance, chromates/dichromates are widely applied for preventing corrosion of aluminium and its alloys.

Although aluminium corrosion and inhibition are old topics and significant researches have already been carried out, there are many unanswered questions. For instance,

- The mechanism of aluminium corrosion has not been completely understood. The exact nature of the chloride interaction with the aluminium oxide film leading to film breakdown remains unclear [Badawy *et al.* 1999; Sehgal, 2000].
- For aluminium alloys, such as AA2024-T3, localised corrosion is thought to initiate at Al-Cu-Mg particles by dissolving Mg and Al leaving copper rich

remnant in the chloride solution. However, the role of this copper rich remnant during further exposure to the chloride solution is still controversial [Buchheit *et al.* 1997; Zhu and van Ooij 2003].

- Corrosion inhibitors such as chromate or dichromate are believed to enhance the passive film, to prevent the initiation of localised corrosion, and to repair any damage in the passive film. However, the mechanism by which chromates/dichromates inhibit corrosion still remains unclear [Akiyama and Frankel 1999; Schmutz and Frankel 1999; Ramsey 2001; Frankel and McCreery 2001]. Chromates/dichromates are generally considered as anodic inhibitors [Rozenfeld 1981; Jeffcoate *et al.* 2000] because they can greatly reduce the local dissolution kinetics of aluminium and its alloys in pits or crevices, owing to the high reversible potential of the Cr(VI)/Cr(III) reaction. On the contrary, it was also reported that the mechanism of localised corrosion inhibition by chromates could be something other than anodic inhibition in the pit or crevice environment [Akiyama and Frankel 1999]. Recent investigations [Frankel and McCreery 2001; Meng *et al.* 2002] indicated that dichromates or its reduction product (Cr_2O_3) reduced pitting corrosion by acting as a cathodic inhibitor and forming a protective film.
- The development of environmentally friendly alternatives to toxic chromates/dichromates is still in its infancy [Cohen 1995; Bethencourt *et al.* 1998]. For instance, although lanthanide salts such as cerium chloride have been found to provide significant inhibition to aluminium corrosion, their mechanism and efficiency require further study.

In order to answer these questions, many traditional electrochemical and analytical

techniques, such as the scanning electron microscope (SEM) and polarisation techniques, have been applied and are still playing important roles in aluminium corrosion and inhibition studies. Equipped with energy dispersive x-ray spectroscopy (EDS), SEM is widely used to characterise very tiny corrosion pits, the corrosion products, the mechanical defects, second phases, inclusions, or other microscale differences on the specimen surface. The relationship between the localised attack and the micro-defects can then be studied conveniently [Blanc *et al.* 1997; Campestrini *et al.* 2000]. Polarisation techniques are also widely used in corrosion study because they can provide electrochemical parameters, such as pitting potential, of materials being studied. Recently, atomic force microscopy (AFM) has been extensively applied in the study of corrosion and its prevention [Schmutz and Frankel 1999; Leblanc and Frankel 2002]. Although these techniques have shown their capabilities in corrosion study, they still have disadvantages. For instance,

- Observation and elemental analysis techniques such as SEM, XPS requires periodic removal of the testing samples from the corroding environment, which is cumbersome and may alter the progress of corrosion.
- As an *in situ* observation method, the AFM can be applied for monitoring the topographical changes during the corrosion process in micro-scales. However, it is unable to provide any direct electrochemical information on the corrosion process. Thus, AFM is usually used in combination with other techniques, such as scanning Kelvin probe force microscopy (SKPFM), which can be used to produce Volta potential distribution maps [Leblanc and Frankel 2002].
- Traditional electrochemical methods such as polarisation techniques usually lack in the ability to provide spatial information on the corrosion process, when they

are used independently. Moreover, they are basically developed on the basis of uniform electrochemical corrosion theory. Thus, they have inevitable limitation in localised corrosion study.

This thesis sets out to address some of unanswered questions by developing and applying a novel technique based on the combined use of the wire beam electrode (WBE) and scanning reference electrode technique (SRET). The WBE in conjunction with SRET method will be used to study the mechanism of pure aluminium AA1100 and aluminium alloy AA2024-T3 corrosion, as well as the mechanism of corrosion inhibitors.

CHAPTER 2

Literature Review: Aluminium Corrosion and Its Inhibition Studies

2.1 Localised Corrosion of Aluminium and Its Alloys

Thermodynamically, aluminium is a very reactive metal as indicated by its position in the electromotive force (emf) series. Its standard reduction potential is approximately -1.66 V vs. standard hydrogen electrode (SHE). Figure 2.1 is a potential-pH diagram (or Pourbaix diagram) of aluminium in water [Shreir *et al.* 1994]. It can be seen that aluminium would undergo general corrosion within the pH range of less than 4, or larger than 8.5 (or ~ 9). Except for in highly acidic or alkaline corrosive environments, as in phosphoric acid or sodium hydroxide, aluminium generally has excellent resistance to general corrosion and gives years of maintenance-free service in most natural environments.

In acidic conditions ($\text{pH} < \sim 4$), aluminium will dissolve as Al^{3+} by reactions such as,

In caustic conditions ($\text{pH} > \sim 9$) aluminium will dissolve as AlO_2^- by reactions such as,

Within the pH range of 4 to 8.5 (or ~ 9), as shown in Figure 2.1, aluminium and its alloys owe their excellent corrosion resistance to the passivity produced by an inert and protective aluminium oxide film, which forms almost immediately when aluminium surface is exposed to air. Passivity is the most important phenomenon that affects the behaviour of aluminium corrosion.

Figure 2.1 Potential versus pH Diagram for Al/H₂O system at 25°C showing the conditions of corrosion, immunity, and passivation [Source: Shreir 1994]

When exposed to an environment in which the oxide films are insoluble (within the passive range), aluminium and its alloys will suffer from localised corrosion at the

weak spots in the oxide films [Davis 1999]. Pitting corrosion is the most common and serious corrosion attack on aluminium alloys, which usually occurs in environments with the presence of aggressive anionic species, such as chloride ions [Wranglen 1972; Frankel 1998]. Mechanisms by which Cl^- ions interact with passive film of aluminium were summarised by Yu *et al.* [Yu *et al.* 2000], i.e. *i*) ion migration/penetration of the oxide, *ii*) adsorption/ion displacement leading to oxide thinning and *iii*) breakdown and repair of oxide. However, the detailed processes of the mechanism by which Cl^- ions initiate pitting corrosion of aluminium are still unclear. For instance, McCafferty deemed that the breakdown of oxide film would involve the transportation of chloride ions through the oxide film; and localised film dissolution or thinning [McCafferty 1995], while Frankel considered that it would be due to breakdown and repair of oxide film [Frankel 1998]. This is due in part to a lack of direct observation of microscopic details of oxide film formation [Sinha and Hebert 2000].

Although the definitive mechanism of chloride ions interact with the passive film has yet to be established, model for aluminium pitting has been provided. It was reported that the pitting of aluminium in chloride-containing solutions follows a similar mechanism to that of the stainless steels [Wranglen 1972; Hatch 1984]. A typical pitting corrosion attack usually involves four stages [Szklańska-Smiałowska 1999]:

- i) Processes occurring on the passive film, at the boundary of the passive film and the solution;
- ii) Processes occurring within the passive film, when no visible microscopic changes occur in a film;
- iii) Formation of so-called metastable pits which initiate and grow for a short period of time below the critical pitting potential and then repassivate (this is an intermediate step in pitting);
- iv) Stable pit growth, above pitting potential.

The fourth stage of pitting corrosion is the most extensively investigated corrosion process. At the fourth stage, aluminium pitting corrosion growth progresses in a manner of autocatalysis, as shown in Figure 2.2. The propagation of aluminium pitting corrosion generally involves several processes, which take place at various locations, such as 'within the pit', 'in the pit mouth', and 'around the pit' [Wranglen 1972].

Figure 2.2 Electrochemical mechanism of pit growth on aluminium, showing its autocatalytic self – stimulating nature [Source: Wranglen 1972]

1. Within the corrosion pit: Preventing repassivation

Enrichment of chloride ions is created in the pit by migration with the corrosion current, which is generated by the pit cell. An acidic solution is generated within the pit, which is caused by the hydrolysis of metal ions, and a consequent local rise in the passivation potential. High conductivity is generated in the

solution, which contains high concentration of salt, in the pit. O_2 supply is limited, which is partly due to low O_2 solubility in the concentrated pit electrolyte.

2. In the pit mouth:

A crust of hydrate is formed, which counteracts the dilution of the pit solution by diffusion and convection and hence strengthens the factors listed above.

3. Around the pit: Preventing general corrosion

Cathodic protection is generated by the corrosion current. Passivation is caused by the formation of alkali in the cathode reaction, particularly in the presence of calcium hydrogen carbonate. More noble metals, such as copper, are deposited on local cathodes, increasing their efficiency, so that the cathode potential within the pit clearly has to be in the active region, which is facilitated by the pit.

The pitting potential principle, i.e. pitting can occur only when potential is above the pitting potential, otherwise, pitting will never occur, establishes the conditions under which metals in the passive state are subject to corrosion by pitting [Kaesche 1963; Bohni and Uhlig 1969; Biloni and Uhlig 1970; Uruchurtu and Dawson 1986]. It has been reported that the critical pitting potential, which is generally associated with pitting initiation, was a function of the concentration of chloride but was independent of the pH of electrolyte [McCafferty 1995].

Pitting potential is used as an important parameter to determine localised behaviour of aluminium. For instance, Davis *et al.* have found that the meta-stable pitting behaviour of pure aluminium with different orientations was followed as a function of potentials below the pitting potential in deoxygenated sodium chloride solution [Davis *et al.* 2000]. Several investigators [Bond *et al.* 1966; Galvele *et al.* 1974; Galvaele and DeMicheli 1970] have used controlled potential techniques to determine pitting potentials of high-purity aluminium in various chloride containing

environments. The results obtained are summarised in Table 2.1.

Table 2.1 Pitting potential determined on aluminium at 25 °C [Bond 1981]

Electrolyte	Materials	Pitting potential vs. SHE (V)
0.1M NaCl	High-Purity Al	- 0.40
0.1M NaCl	High-Purity Al	- 0.46
0.5M NaCl	High-Purity Al	- 0.50
1M NaCl	High-Purity Al	- 0.48
1M NaCl	High-Purity Al	- 0.52
0.1M NaCl	Al-2.4 Mg	- 0.41
0.1M NaCl	AL- 0.2 Cu	- 0.44
0.1M NaCl	Al-4Cu (solution treated)	- 0.46

Note: SHE = standard hydrogen electrode

Metallic alloying elements, which are commonly added to aluminium in order to improve its properties such as mechanical strength, make aluminium alloys such as AA2024-T3 more susceptible to localised corrosion. The enhanced corrosion susceptibility of aluminium alloy compared to pure aluminium is thought to be due to local galvanic cells that are established by virtue of heterogeneous redox reactivity associated with the presence of the intermetallic particles [Buchheit *et al.* 1997; Blanc *et al.* 1997; Chen *et al.* 1996]. Besides aluminium matrix, there are two, based on composition, major types of intermetallic particles (phases/inclusions) in AA2024-T3, i. e. Al-Cu-Mg (S phase) and Al-Cu-Fe-Mn particles. Buchheit [Buchheit 1995] has summarised the corrosion potentials of intermetallic phases in aluminium alloys, as shown in Table 2.2. For AA2024-T3, Al₂CuMg has a corrosion potential of -0.890 V vs. SCE in 1.0 M sodium chloride solution [Urushino and Sugimoto 1979], which is thermodynamically active. In addition to the two intermetallic phases, more phases in AA2024-T3 alloy have also been reported, i.e. Al-Si-containing, and Al-Cu-containing (θ phase) particles [Zhu and van Ooij

2003]. It has been reported that the Al-Cu-Fe-Mn containing and Al-Si-containing particles are both cathodic towards the Al matrix [Buchheit 1995; Obispo *et al.* 2000]. Mueller and Galvele [Mueller and Galvele 1977] have reported that copper additions to aluminium can result in improvements in pitting resistance when copper is in a solid solution, however, when particles of the intermetallic θ -phase (CuAl_2) formed, the resistance to pitting decrease to the range of aluminium alloyed with little copper.

Table 2.2 Corrosion potential for intermetallic compounds in aluminium alloys [Buchheit 1995]

Phase	Stoichiometry	Corrosion potential (V_{SCE})	Environment	Aeration
S	Al_2CuMg	- 0.89	1.0 M NaCl	Open to air
S	Al_2CuMg	- 0.92	0.5 M NaCl	N_2 sparged
S	Al_2CuMg	- 0.89	53 g/L NaCl + 3 g/L H_2O_2	Open to air
θ	Al_2Cu	-0.76	1.0 M NaCl	N_2 sparged
θ	Al_2Cu	- 0.70	0.5 M NaCl	Open to air
θ	Al_2Cu	- 0.59	1.0 M NaCl	N_2 sparged

All potentials are determined at 20-26 °C

All the research works regarding aluminium alloys, including AA2024, 5083, 6056, and 6061, show that the existence of the intermetallic particles in the alloys is the main reason for localised corrosion. Composition specifications for AA2083, 6056 and 6061 were given in Table 2.3. For aluminium alloy AA2024-T3, it was regarded that S phase particles, the most active intermetallic particles in this alloy, was anodically polarised by the surrounding α -Al matrix phase [Buchheit *et al.* 1999]. The particle then dealloyed under anodic polarisation, leaving behind a porous copper-rich particle remnant. Many researches have shown that S phase particles were the preferential sites where corrosion usually initiated by means of

dealloying of Mg and Al from S phase particles [Buchheit *et al.* 1997; Zhu and van Ooij 2003; Guillaumin and Mankowski 1999; Dimitrov *et al.* 2000].

Table 2.3 Composition Specifications for Aa5083, 6056 and 6061

Component	Al	Cr	Cu	Fe	Mg	Mn	Si	Zn
AA5083	92.4-95.6	0.05-0.25	Max0.1	Max0.4	4-4.9	0.4-1	Max0.4	Max0.25
AA6056	93.6-97.7	Max0.25	0.5-1.1	Max0.5	0.6-1.2	0.4-1	0.7-1.3	0.1-0.7
AA6061	95.8-98.6	0.04-0.35	0.15-0.4	Max0.7	0.8-1.2	Max0.15	0.4-0.8	Max0.25

Recently, research has been carried out to get insight into the effects of intermetallic particles on the initiation mechanism of pitting of AA2024-T3 by investigations of processes at the micro- and nanometer scales. It has been found that no attack occurred at areas containing only Al-Cu-Fe-Mn particles or no Al-Cu-Fe-Mn particles [Liao *et al.* 1999; Suter and Alkire 2001; Leblanc and Frankel 2002]. Also, the pitting mechanism dramatically changed from the dissolution of AlCuMg inclusions to the attack of the matrix, as the ratio of noble Al-Cu-Fe-Mn particles increased with respect to the surrounding exposed area. When the studies carried out using a sample containing no visible inclusions (i.e. only aluminium matrix), pitting could only be observed at very high potential. Thus, it was concluded that the pitting potential of bulk samples was determined by the most active inclusions.

The kinetics of pitting corrosion of the AA2024 and of the AA6056 has been studied by determining the mean pit propagation rate of these materials under different conditions. It was found that for whatever material (AA2024 or AA6065); the mean pit propagation rate varied linearly with the logarithm of the chloride concentration [Blanc and Mankowski 1998]. Besides in sodium chloride solution, AA2024-T3 has also been studied in several other solutions, e.g. nitrate solutions [Blanc *et al.* 2003], hydrochloric acid solutions [Kowal *et al.* 1996], and sulfate solutions [Kolics *et al.* 1998]. Moreover, strong anisotropy of localised corrosion

was found in AA2024-T3 [Zhang and Frankel 2000; 2002]. They found that the anisotropy of growth kinetics was different for various forms of AA2024-T3 having different microstructures.

In general, taking intermetallic into consideration, two mechanisms for the corrosion of aluminium alloys, in particular AA2024-T3, in chloride containing solution, have been reported:

i) Corrosion mechanism based on galvanic corrosion

The copper-rich particle remnant formed by the dealloyed S phase particle was supposed to behave as efficient cathode with respect to the matrix leading dissolution of the matrix surrounding these particles [Buchheit *et al.* 1997; Guillaumin and Mankowski 1999; Dimitrov *et al.* 2000]. These particles may also anodically dissolve to form Cu clusters which dispersed into the corrosive environment and redeposited as copper cathodes on aluminium surface at later stages of exposure [Buchheit *et al.* 2000]. Hence, galvanic corrosion system could be established between the surrounding aluminium matrix and the redeposited copper. The establishment of such a galvanic system would then result in the dissolution of aluminium matrix, which was around the copper-rich remnant.

ii) Corrosion mechanism based on cathodic corrosion

In another research, the proposed copper-rich remnants in the galvanic corrosion based mechanism have not been found to turn into efficient cathodes by Zhu and van Ooij [Zhu and van Ooij 2003], and Leblanc and Frankel [Leblanc and Frankel 2002]. In their experiments, no severe corrosion was found to occur at the aluminium matrix surrounding the copper-rich remnants. Thus, alternative mechanism of aluminium

dissolution in the vicinity of S phase particles is then proposed [Zhu and van Ooij 2003]. When the dealloying of Mg and Al occurs, the accompanying cathodic reactions, water reduction and oxygen reduction, are most likely to take place on the aluminium matrix at the periphery of the S phase particles [Vukmirovic *et al.* 2002; Zhu and van Ooij 2003]. Hydroxide ions (OH^-) could be generated and then the pH value could be increased locally by this process. Once the local pH exceeds 9 (equilibrium pH of aluminium oxide), the surrounding aluminium oxide layer on the aluminium matrix would no longer survive and would dissolve according to

Simultaneously, the bare aluminium matrix underneath would be oxidized to form a new layer of Al oxide, releasing hydrogen gas by the reaction

It should be noted that the dissolution of aluminium oxide is simply a chemical dissolution, whereas the formation of the aluminium oxide is an electrochemical process in which electrons transferred from anode, where aluminium dissolves and releases electrons, to the cathode, where the electrons are consumed [Moon and Pyun 1997]. This mechanism of aluminium dissolution in an alkaline medium, as shown in Figure 2.3, was usually called “cathodic corrosion” of aluminium [van der Ven and Koelmans 1976; Desouc *et al.* 1990; Takahashi *et al.* 1994].

Figure 2.3 (a) dealloying and local alkalisation, and (b) cathodic corrosion of the surrounding Al matrix [Source: Zhu and van Ooij 2003]

Although localised corrosion initiating by preferential dissolution of Mg and Al at S phase particles in AA2024 is a general accepted fact, the role of copper-rich remnant, which is formed by the dissolution of Mg and Al at S phase, in the subsequent corrosion process is still in a controversy. It does deserve further study to clarify the dealloyed S phase and the applicability of the two mechanisms discussed above.

2.2 The Inhibition of Aluminium Corrosion

Corrosion inhibitors are chemicals (organic and inorganic) that are added in small amounts to a corrosive environment to reduce or stop corrosion. Inhibition of aluminium corrosion has been applied for many years, in various environments, using different inhibitors and different application methods. Of all the chemicals, chromates/dichromates are the most widely used for protecting aluminium from localised corrosion, especially in near-neutral environments containing aggressive anions such as chloride [Akiyama and Frankel 1999; Ramsey and McCreery 1999;

Szklarska-Smialovska 1999; Jeffcoate *et al.* 2000; Frankel and McCreery 2001; Gancs *et al.* 2002].

Chromate or dichromate is an important corrosion inhibitor that has been used to protect both ferrous and nonferrous metals against corrosion [Rozenfeld 1981b; Ramsey *et al.* 2001]. Currently, these compounds are widely used as inhibitors or incorporated in anticorrosive, pretreatments of aluminium alloys due to their extreme effectiveness in inhibiting aluminium corrosion. The forms in which they can be used include: *i*) Chromate containing conversion coatings, *ii*) Chromate containing solutions.

In spite of the extensive use of chromates and the effective inhibition on corrosion, particularly for localised corrosion, the full details of precisely how they work are still not known [Bethencourt *et al.* 1998; Ilevbare *et al.* 2000]. Major efforts are being made to elucidate the inhibition mechanism of chromium species, particularly the activity of Cr(VI) as a cathodic or anodic inhibitor, or both [Tidblad and Lindbergh 1991; Sehgal *et al.* 1998; 2000; Schmutz and Frankel 1999; Ilevbare and Scully 2001]. The mechanism of corrosion inhibition by which chromates operates remains unclear [Akiyama and Frankel 1999; Schmutz and Frankel 1999; Ramsey 2001; Frankel and McCreery, 2001].

Major research work has been focused on the study of effects of chromate on aluminium alloys AA 2024-T3 [Ilevbare *et al.* 2000; Kolics *et al.* 2001; Brown and Kobayashi 2001; Zhao *et al.* 2001; Campestrini *et al.* 2001; Clark *et al.* 2002]. Chromates are generally considered as anodic oxidizing inhibitors [Lusdem and Szklarska-Smialovska 1978; Rozenfeld 1981a]. Rozenfeld and other researchers classified chromates/dichromates as anodic inhibition because they could greatly reduce the local dissolution kinetics of aluminium and its alloys in pits or crevices, owing to the high reversible potential of the Cr(VI)/Cr(III) reaction [Rozenfeld

1981b; Jeffcoate *et al.* 2000]. On the contrary, it was found that the addition of dichromate ions was not able to suppress the active crevice dissolution of aluminium in chloride-containing solutions [Akiyama and Frankel 1999]. Thus, it was concluded that the mechanism of localised corrosion inhibition by chromates should be something other than anodic inhibition in the pit or crevice environment. In recent years, considerable evidence has been found that dichromates or its reduction product (Cr_2O_3) reduced pitting corrosion by acting as a cathodic inhibitor and forming a protective film that inhibited localised corrosion [Frankel and McCreery 2001; Meng *et al.* 2002]. A recent research showed that chromate did not effectively reduce the rate of localised corrosion propagation in aluminium or aluminium alloys [Sehgal *et al.* 2000]. It has been established that chromate ions increased the pitting potential of aluminium alloys in chloride media and reduced the rate of pit nucleation and growth [Frankel and McCreery 2001]. This has been attributed to chromates' ability to inhibit the incorporation of corrosive species (e.g. Cl^- ions) into the oxide film [Jeffcoate *et al.* 2000]. Frankel and McCreery [Frankel and McCreery 2001] has also summarised the reasons for that chromate was an extremely effective corrosion inhibitor for aluminium alloys particularly AA2024: *i*) Chromate is mobile in solution and migrated to exposed areas on the aluminium alloy surface; *ii*) Formation of monolayer of Cr (III) species due to chromate adsorption on the active sites of the surface; *iii*) The presence of this layer is effective in reducing the activity of both cathodic sites (Cu-rich intermetallic particles) and anodic sites in the matrix or at Al_2CuMg (S phase).

Chromate conversion coatings (CCCs) on aluminium and its alloys are known to be very effective in protecting against localised corrosion and promoting paint adhesion. This is due to electrochemical processes involving oxidation of aluminium (the destabilization of the passive oxide film by fluoride) and reduction of Cr(VI) to Cr(III) by the exposed aluminium [Akiyama and Frankel 1999; Zhang *et al.* 2002; Zhao *et al.* 1998]. Findings of recent studies [Frankel and McCreery 2001;

Akiyama and Frankel 1999; Zhang *et al.* 2002; Zhao *et al.* 1998] showed CCCs to be a mixture of chromium oxides and other components from the coating bath and substrate. These coatings have been shown to contain both Cr(VI) and Cr(III), with relative concentrations depending on the pre-treatment procedure. It has been found that Cr(VI) ions are absorbed by AlO_x surfaces, to form both Al(III)-Cr(VI) mixed oxide [Ramsey and McCreery 1999; Zhao *et al.* 2001] and Cr(III)-Cr(VI) mixed oxide [Xia *et al.* 2000]. Release of Cr(VI) from CCCs to effect “self-healing” has been found to be one of the major reasons for the efficiency of CCCs to protect aluminium and its alloys [Frankel 2001]. The “self-healing” mechanism of CCCs on AA2024-T3 is shown in Figure 2.4. It can be seen that the release and migration of Cr(VI) from CCCs is responsible for the critically important “self-healing” action.

Figure 2.4 Self-healing mechanism of CCCs on AA2024-T3 [Source: Frankel 2001]

The mechanism shown in Figure 2.4 is in agreement with two phenomena observed by Szklarska-Smialowska [Szklarska-Smialowska 1999] after aluminium was immersed in neutral chromate solutions, i.e. *i*) adsorption of chromates, and *ii*) partial reduction of chromates. Passive films formed on aluminium in the presence of chromate ions were found to be composed of hydrated Cr(III) and Al(III) oxide as

well as significant amount of adsorbed Cr(VI) species. The rapid uptake of chromium by aluminium oxide was assumed to be associated with the reduction of $\text{Cr}_2\text{O}_7^{2-}/\text{CrO}_4^{2-}$ at the tips of flaws in the surface film; conversely, a more gradual uptake was associated with the penetration of $\text{Cr}_2\text{O}_7^{2-}/\text{CrO}_4^{2-}$ in the outer layer of the film.

Chromates/dichromates are highly toxic and carcinogenic, and are major environment hazards. Thus, ecological alternatives to chromates are being investigated. Lanthanide compounds, especially cerium chloride, have been considered as economically competitive alternative to chromates.

Lanthanides chlorides have been found to be cathodic inhibitors for aluminium alloys in neutral sodium chloride solution [Bethencourt *et al.* 1997; Aldykewicz Jr. *et al.* 1995]. Bethencourt *et al.* found lanthanide salts could act as pitting corrosion inhibitors as well as uniform corrosion inhibitors. Cerium chloride is regarded to inhibit aluminium corrosion by means of the formation of cerium-rich films [Davenport *et al.* 1991]. Bethencourt *et al.* found cerium islands over the cathodic precipitates, $\text{Al}_6(\text{MnFe})$. They proposed that the blockage of the cathodic sites decreased the available cathodic current and, therefore, reduced the overall corrosion rate [Bethencourt *et al.* 1998]. OH^- anions, created over the cathodes due to cathodic reaction, can produce areas with a local alkalinity that favours the cerium precipitation. However, it has been found that when aluminium was exposed to both weak and strong alkaline solutions, cerium species can function as anodic inhibitors [Crossland *et al.* 1998]. Cerium has also been used to generate cerium oxide/hydroxide coatings, which contain Ce(III) and Ce(IV) species [Davenport *et al.* 1996; Hinton *et al.* 1986]. Hinton *et al.* proposed that the presence of H_2O_2 was necessary for the oxidation of Ce(III) to Ce(IV) [Hinton *et al.* 1989]. On the other hand, Arenas *et al.* [Arenas *et al.* 2002] found that the inhibitor efficiency of cerium chloride decreased with decrease in inhibitor concentrations. They suggested that

in low concentration inhibitor solutions, the predominant corrosion inhibition mechanism was inhibitor diffusion control, while in higher concentrations, the corrosion mechanism changed from diffusion to activation control. Copper rotating disk electrode (RDE) was employed by Kendig *et al.* to characterise the oxygen reduction reaction and its inhibition by Cr(VI) and Ce(III) [Kendig *et al.* 2002]. They concluded that the inhibition of oxygen reduction by Ce(III) was less efficient and more slowly responding than inhibition provided by comparable activities of Cr(VI). Other researchers have also studied the corrosion protection provided by lanthanide compounds for steel [Isaacs *et al.* 1991; Lu 1993], zinc [Hinton *et al.* 1989; Kunitsugu Aramaki 1989] or aluminium [Mansfeld *et al.* 1990].

However, there are many unanswered questions regarding the inhibition mechanism and efficiency of lanthanide inhibitors. For instance, the mechanism of lanthanide salts, especially cerium chloride, as inhibitors for aluminium corrosion is still unclear. Although the polarisation curve of aluminium alloy in cerium chloride containing solution revealed cathodic inhibition characteristics and some results obtained using SEM or XANES (X-Ray Absorption Near-Edge Spectroscopy) showed the preferential formation of cerium rich film on the cathodic intermetallic particles in Al-Cu- alloys such as AA2024 [Davenport *et al.* 1991], its mechanism still deserves further study. For example, almost all the researches that have been performed focused on the effectiveness of cerium chloride in inhibiting the initiation of corrosion, little has been done to understand how it works after corrosion has occurred.

Other possible alternatives to chromates, such as molybdate, have also received attention as a replacement for chromate conversion coatings. Molybdate mimics chromate in a variety of applications but it exhibits significantly lower toxicity. However, it has been found that the effectiveness of chromates is still superior over that of molybdate for AA2024 in sodium chloride solutions [Badawy *et al.* 1999;

Arenas *et al.* 2001]. It is suggested that inhibitive nature of the molybdate anions might be due to reduction of Mo(VI) to Mo(IV) during film formation [Augustynski 1978]. However, the clear mechanism by which molybdate controls passivating behaviour is still a matter of discussion [Emregul and Aksut 2003].

Although a lot of works have been carried out for finding environmentally friendly alternatives to the efficient but toxic chromates/dichromates, many problems remain unsolved. The development of viable alternatives to chromates is still in its infancy [Cohen 1995; Bethencourt *et al.* 1998].

2.3 Traditional Technologies for Aluminium Corrosion Study

Many laboratory techniques have been developed and utilised in the study of aluminium corrosion. These techniques can be generally classified into two major types: *i*) non-electrochemical techniques such as weight loss measurements, visual inspection, observation using microscope or scanning electron microscope (SEM), metallographic examination, nondestructive inspection; and *ii*) electrochemical techniques such as polarisation measurements and electrochemical noise analysis.

Non-electrochemical Techniques

Visual examination of the corroded metal surface is the most commonly applied method for corrosion studies. Visual observation can be done with or without a magnifying glass. A visual examination of the metal surface can determine the sizes and shapes of corrosion damages such as pits. When the corrosion products are removed, a more detailed examination can be carried out through a microscope to determine the actual shapes and depths of pits.

Weight loss measurement is a conventional method to evaluate corrosion rate by determining the difference of the metal mass before and after corrosion. Obviously, this method cannot provide instantaneous corrosion rate information, moreover, if the mass changes are too small, it will be very difficult to determine the weight loss accurately [Blanc *et al.* 2003; Blücher *et al.* 2003].

SEM, usually equipped with EDS facilities, can be used to characterise very tiny pits due to its high resolution. Corrosion products, mechanical defects, second phases, inclusions, or other microscale differences on a specimen surface can be easily observed and analyzed [Guillaumin and Mankowski 1999]. The relationship between the localised attack and the micro-defect can be studied conveniently [Blanc *et al.* 1997; Campestrini *et al.* 2000].

Other techniques for surface chemical analysis such as X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) have also been used widely in the study of corrosion and its inhibition [Koudelkova *et al.* 1977; Bairamow *et al.* 1985; Hughes *et al.* 1996; Natishan *et al.* 1999; Badawy *et al.* 1999; Yu *et al.* 2000; Kolics *et al.* 2001a and b; Chidambaram *et al.* 2003; Wang *et al.* 2004]. XPS can be used to obtain chemical information of corrosion sample with only minimum radiation damage of the sample surface, however the chemical information is averaged over a large surface area and point analysis is often difficult [Leidheiser 1978].

Although non-electrochemical techniques discussed above can provide very valuable information on corrosion, and have been being applied in aluminium corrosion studies [Kolics *et al.* 1998; Kendig *et al.* 2001; McCafferty 2003; Garcia-Vergara *et al.* 2004], they have certain limitations. *i)* Corrosion is inherently dynamic, while the observation or surface analysis techniques are essentially static in nature. *ii)* Removal of specimen is required. For instance, optical or scanning electron

microscopic observation methods require the removal of the specimen from the electrolyte and thus will interrupt the corrosion process. It has been reported that drying or loss of absorbed water [Hopkins 1995] and transferring sample can result in a change in surface chemistry or surface structure [Leidheiser 1978]. *iii)* The analysis process itself can change the composition of the specimen surface. For instance, damage and inhomogeneities may be caused by the sputtering process, which is usually applied to probe past the topmost surface of a specimen [Hopkins 1995].

As an *in-situ* technique, atomic force microscopy (AFM) is receiving considerable attention in the field of surface science and engineering because of its ability to image surfaces, such as surface inhomogeneities, grain boundaries, exceedingly fine precipitates, or inclusions etc. with atomic scale resolution [Shimizu *et al.* 1997]. High lateral resolution of AFM makes it a powerful technique for the analysis of surface structures of the sample under study, either conducting or non-conducting. Recently, AFM has been used to study the corrosion and inhibition of aluminium because of its potential in revealing shape evolution at the nano-scale level during corrosion [Rynders *et al.* 1994; Kowal *et al.* 1996; Schmutz and Frankel 1999; Campestrini *et al.* 2001; Suter and Alkire 2001; Kendig *et al.* 2001; Leblanc and Frankel 2002]. In combination with other techniques, the AFM was used to generate considerable understanding of the corrosion behaviour of aluminium alloy AA2024. For example, scanning Kelvin probe force microscopy (SKPFM) has been used to produce maps of the Volta potential distribution, and meanwhile AFM was used to examine the topographical change over surfaces of AA2024-T3 in air [Schmutz and Frankel 1998 a and b; 1999].

Electrochemical Techniques

Electrochemical techniques are widely used in corrosion study. Many corrosion

tests and standards regarding electrochemical techniques have been developed. Generally, electrochemical methods can be classified into: *i*) electrochemical methods for the study of uniform corrosion, such as Tafel extrapolation, polarisation resistance, electrochemical impedance; *ii*) electrochemical methods for the study of the passivity and localised corrosion, including cyclic potentiodynamic polarisation, potentiostatic and galvanostatic methods; *iii*) electrochemical evaluation of protective coatings and films, including electrochemical impedance spectroscopy (EIS) [Scully 1995].

Breakdown of passive film on materials, which is regarded as the main reason for pitting corrosion, is widely studied. Epelboin and Keddam have reviewed the electrochemical techniques for the study of passivity and localised corrosion, which includes steady-state approach, large amplitude perturbations, small amplitude perturbations, and some particular techniques [Epelboin and Keddam 1978]. The most commonly applied electrochemical method of determining pitting corrosion sensitivity is to determine pitting potential by measuring anodic polarisation curve. This curve can be obtained by means of two methods, i.e. potential control method (using a potentiostat device) and current control method (using a galvanostat device). For example, potentiostatic measurement [Kendig *et al.* 2001; Lunt *et al.* 2002] can be carried out by either *i*) stationary: holding the specimen at each assigned potential until a constant current is established, or *ii*) potentiodynamic: changing the potential continuously at a constant rate. Typical results of this measurement are illustrated in Figure 2.5. Using this technique, pitting nucleation potential (E_{np} on the curve) and protection potential (E_{pp}) can be attained.

Figure 2.5 Anodic polarisation by potentiostatic measurements [Source: Szklarska-Smialowska 1986]

Another electrochemical method that has been widely used in assessing resistance of metals to localised corrosion is cyclic potentiodynamic polarisation measurement [Brennett 1937; Hospadaruk and Petrocell 1966; Pourbaix *et al.* 1963; Defranoux 1963]. During cyclic polarisation, metals are polarised from active to more noble potentials until some critical values have been reached, and subsequently polarisation has been reversed towards more active potentials. The technique has been applied to the study of initiation of pitting and crevice corrosion, propagation of existing pits and crevices, and galvanically induced localised corrosion [Pourbaix 1970; Babonian 1972; Babonian and Hanyes 1974]. Cyclic polarisation scan starts at corrosion potential (E_{corr}) towards the more noble potential direction. During this process, breakdown of the surface film of the passive metal occurs at critical potential (E_{np}), which is indicated by a rapid increase in current. When corrosion current reaches the limit of 5 mA, scan is reversed until repassivation occurs at potential E_{pp} (hysteresis loop is complete or corrosion potential is reached). Typical curve of the cyclic polarisation measurement is shown in Figure 2.6.

Figure 2.6 Representative cyclic potentiodynamic polarisation curves

[Source: ASTM G 61-78]

The polarisation techniques do provide some electrochemical information on corrosion process. They are very useful in studying corrosion system in some extent, and are still being used widely [Kiourtsidis *et al.* 1999; Dimitrov *et al.* 2000; Dursun *et al.*; Blanc *et al.*; Zhang and Frankel 2003]. However, the electrochemical parameters, such as potential or current density, obtained in such measurements are a mixed or average value. Since the techniques are based on uniform corrosion theory, local electrochemical parameters and their spatial distributions cannot be obtained using these techniques. Such shortcomings of polarisation techniques do limit their applications in localised corrosion study. Thus, these techniques are seldom used independently in studying localised corrosion systems. They are usually used in combination with other techniques, such as microscopic observation of corroded sample surface.

Another electrochemical method for corrosion study is electrochemical noise analysis (ENA). Fluctuations in the electrical quantities of electrochemical systems, such as cell current and electrode potential, are referred to as electrochemical noise (EN), analogous to the use of the word ‘noise’ to indicate random, incoherent acoustic or electrical fluctuations. Noise analysis has been applied increasingly to electrochemical systems, particularly in corrosion science and engineering [Cottis *et al.* 1998; Alawahdi and Cottis 1999; Gonzalez-Rodriguez *et al.* 2000; Aballe *et al.* 2002]. The measurement of electrochemical noise for corrosion studies is first described by Iverson [Iverson 1968], although Tyagai examined EN in electrochemical engineering at about the same time [Tyagai 1971; 1974]. The electrochemical noise of the corrosion system is often regarded as a random (stochastic) phenomenon coupled to deterministic kinetics. Several investigators [Bertocci 1980; 1981; Bertocci and Kruger 1981] deemed these fluctuations have some association with the initiation of localised corrosion. It was later realized that fluctuations in electrode potential could be used in corrosion studies [Dawson 1983]. At first, the researchers [Steward and Williams 1992] were concerned with a detailed investigation of individual potential transient events, notably those associated with metastable pitting. Hladky and Dawson reported that the localised corrosion such as pitting and crevice had quite distinct noise “signature” and such corrosion attack can be detected within seconds of their initiation [Hladky and Dawson 1981].

Electrochemical noise measurement is usually carried out in a free corrosion condition and does not need to apply a perturbation on the test system by an externally imposed polarisation, which could lead to inevitable changes of the system-specific properties. The typical experimental arrangement for electrochemical noise recording is shown in Figure 2.7. Figure 2.8 shows a typical result regarding corrosion study using electrochemical noise measurement.

Figure 2.7 Schematic illustration of EN recording [Source: Tan *et al.* 1996]

Figure 2.8 (a) Electrode noise output during pit initiation period and (b) D. C. component during pit initiation period [Source: Hladky and Dawson 1981]

This technique has been utilised to study localised corrosion by some researchers [Legat and Zevnick 1993; Tan *et al.* 1998], in particular, Uruchurtu and Dawson have

applied reciprocal frequency ($1/f$) electrochemical noise for the detection of pitting corrosion and the activation of pure aluminium in chloride media [Uruchurtu and Dawson 1986]. Uruchurtu and Dawson carried out noise measurements in neutral and alkaline solutions with and without chloride ion addition in order to compare the noise response from general and pitting corrosion. The influence of indium and mercury ions present in chloride solution on the activation of aluminium was also considered. The spectral density plots they obtained seemed to be able to characterise the type of attack and provide a means of detecting the presence of pitting corrosion. However, the application of EN as a tool of detecting localised corrosion is still a controversial topic. Tan *et al.* [Tan *et al.* 1997] has reviewed some unsolved problems of ENA on localised corrosion studies.

2.4 New Developed Technologies for Aluminium Corrosion Study

Conventional electrochemical methods are based on a uniform corrosion mechanism and a one-piece electrode, which can only detect mixed or averaged electrochemical parameters over the one-piece electrode surface and cannot measure electrochemical parameters from a chosen location of the electrode surface. Some relatively new technologies, such as the Wire Beam Electrode (WBE) and the Scanning Reference Electrode Technique (SRET), have been developed in attempt to overcome this problem.

The Scanning Reference Electrode Technique (SRET)

Since localised corrosion always involves anodic and cathodic reactions that are separated distinctly, there must be current flowing from the anodic area to the cathodic area in the electrolyte. The flow of electrons within the metallic phase does not involve significant ohmic potential differences due to the high conductivity

of the metal. However, the flow of currents within the aqueous phase, carried by ions, is associated with small potential changes between the anodic and cathodic areas. The distributions of potential and ionic current in solution can be determined theoretically from the Laplace equation:

$$\nabla^2 E = 0$$

and ohm's law:

$$i = -\kappa \nabla E$$

Where E is the electrical potential, i is the current and κ is the solution conductivity. Figure 2.9 illustrates the schematic of the flow of current from a localised anode to surrounding cathodes and the equipotential lines around the localised electrode. The product of the polarisation resistance ($\Delta V / \Delta i$) and the electrolyte conductivity has the dimension of length as expressed by the following equation [Isaacs and Vyas 1981]:

$$L = \kappa \Delta V / \Delta i$$

This equation has been used to determine the potential variations in the corrosion systems [McCafferty 1977]. The resolution of the SRET is dependent not only on the proximity of anodic and cathodic sites, but also the magnitude of the corrosion current. Thus, if the flow of current is large enough, the variation in potential could be detected. By scanning a “passive” reference probe with a fine capillary tip parallel and in close proximity to the metal surface, the potential distribution in the solution can be measured. As shown in Figure 2.10, a typical probe arrangement utilised in the SRET consists of two platinum tips, of which their diameter is in the order of one to five micrometers. These tips are housed within a single unit in

closed lateral proximity, but spaced vertically from each other by a few millimetres. The probe moves normally in order to build up two dimensionally resolved data. As the probe scans over the metal surface, there will be an IR drop between the two tips of the probe [Isaacs and Vyas 1981], where I stands for the corrosion current flowing in the electrolyte and R is the resistance of the electrolyte.

Figure 2.9 (a) Current paths in the electrolyte, b) equipotential lines in the electrolyte
[Source: Isaacs and Vyas 1981]

Figure 2.10 Schematic illustrations of the probe tips and the SRET measurement

Representative results obtained from a typical localised corrosion system using SRET measurement are shown in Figure 2.11. The SRET map in Figure 3.3 was

measured using an SP100 SRET system (EG & G Company, USA) and presented as iso-potential contour maps. The values shown in the SRET map are the potential variations caused by the corrosion current flowing from anode to cathode. On the SRET map, the location with negative potential value corresponds with the anodic site (the more negative the potential value, the larger the anodic current value), while that with positive potential value corresponds with the cathodic site.

Figure 2.11 A sample map of SRET measurement

[Source: Johnson and Sargeant 2002]

The SRET has been applied to the study of localised corrosion by many researchers [McCafferty 1977; Mills *et al.*; Akid 1995; Wilde and Williams 1970; Isaacs and Vyas 1981]. Isaacs has studied the pitting of type 304 stainless steel in ferric chloride solution using SRET [Isaacs 1974]. The change in the number of active pits was studied as a function of time and surface preparation, and the active and repassivated pits were separated using the SRET. Isaacs has also studied pitting of stainless steel in sodium chloride solutions under potentiostatic conditions using the SRET [Isaacs and Vyas 1981]. In that work, the voltage values detected by SRET over pits were summed up, and the sum was found to be linearly related to the applied polarisation

current. Akid and Mills [Akid and Mills 2001] have used the SRET to investigate the pitting initiation, surface film breakdown, as well as the inhibition of a tempered martensite medium/high strength steel within artificial seawater. Ballanger and Rameaua have used the SRET to show the formation of anodic and cathodic micro-cells on AISI 630 stainless steel due to localised pitting corrosion in the presence of a TiN coating [Bellanger and Rameaua 1995].

Besides pitting corrosion, SRET has also been used in the study of various other forms of localised corrosion such as stress corrosion cracking (SCC) [Allah-karam *et al.* 2001; Isaacs and Vyas 1981], galvanic corrosion [Akid and Mills; McMurry 2001], intergranular corrosion [Isaac 1981], as well as corrosion preventions such as organic coatings [Mills *et al.* 2000; Maile *et al.* 2000], anodic and cathodic corrosion inhibitors [Bellanger and Rameaua 1995; Powell *et al.* 1999]. On the basis of SRET, a new laboratory test for the evaluation of the delamination resistance of coatings has been developed [Maile *et al.* 2000]

SRET is an *in-situ* technique, which allows real-time localised electrochemical activity to be imaged and quantified. However, since the sensitivity of SRET is highly dependent on corrosion current value, electrolyte conductivity and the probe proximity over corrosion sites, it has limitations in studying corrosion system that only generate small corrosion currents or that have anodic and cathodic sites not well separated. Obviously, the SRET only responds to potential variations in the solution, which are associated with the flow of current and do not relate directly to the potentials of the metal surface. For kinetics studies, it is necessary and important to calibrate the SRET to quantitatively relate the potential to local corrosion current. [Trethewey *et al.* 1993; McMurry *et al.* 1996; Powell *et al.* 1999; McMurry 2001].

A similar technique, namely scanning vibrating electrode technique (SVET), was

also widely used in corrosion studies [Franklin *et al.* 1991; 1992; Worsley *et al.* 2001; Vuillemin *et al.* 2003; Battocchi *et al.* 2005]. The main difference between the SRET and SVET was that SRET was generally used in detecting potential variations caused by corrosion current in the electrolyte, while SVET was basically utilised for mapping anodic and cathodic currents in electrolyte over the corroding sample.

The Wire Beam Electrode (WBE)

The WBE is a newly developed electrode that divides a non-uniform large electrode area into many small parts. It is most commonly made by binding a large number of metal wires together (usually 100 metal wires) using epoxy resin. Each wire in the WBE is insulated from its neighbours with a very thin epoxy layer, constituting a mini-electrode (or mini-sensor) and acting as a corrosion substrate. The array of addressable wires is electrochemically integrated by connecting all wire terminals [Tan 1998; 1999; 2000; Tan *et al.* 2000]. A typical arrangement of a WBE is illustrated in Figure 2.12.

Figure 2.12 Schematic of the design of the WBE

The WBE was initially designed for detecting localised defects in organic coatings films [Tan 1991; Tan and Yu 1991; Wu *et al.* 1995] and in anti-rust oil films. The WBE results on organic coatings showed good correlation with others' work [Mills and Mayne 1981; Mayne 1952; Kinsella and Mayne 1969] and visual observation. Using the individual resistance of the mini-sensors within a WBE rather than the overall resistance, WBE technique overcame the problem of poor reproducibility and reliability of conventional electrochemical measurements of corrosion under organic coatings.

The key ideas of the WBE concept are (i) to simulate a one-piece electrode using an electrochemically integrated electrode array, and (ii) to assume each wire surface is electrochemically uniform even if the whole electrode surface is electrochemically non-uniform [Tan 1999; Tan *et al.* 2000]. These assumptions are reasonable in some aspects of localised corrosion study, since the surface area of each wire is so small compared with the whole electrode. This allows traditional electrochemical theories and techniques to be applied to each individual wire in a WBE [Tan 1998; Tan *et al.* 2000].

Galvanic currents, which can be easily measured by inserting an ammeter into the WBE system, flow between the wires in the WBE, if all the wire terminals are connected together in a corrosive solution, as shown in Figure 2.13 (a). In the corrosive media, some of the wires behave as anodes and others as cathode. It reflects a multi-electrode system where every wire is polarised by other wires and an overall system potential (E_{sys}), which can be measured using a voltameter via a reference electrode (RE), is achieved [Tan 1998].

Figure 2.14 Evans plot illustrating the polarisation of wire k in a WBE corrosion system [Source: Tan 1998]

The overall anodic corrosion current of wire “k” can be expressed as:

$$I_{ka} = I_{gk} + I_{kc} \quad (2.1)$$

At E_{sys} , the anodic reaction current can be written, on the basis of the Butler-Volmer equation, as:

$$I_{ka} = I_k \exp [2.3 (E_{sys} - E_k) / b_{ak}] \quad (2.2)$$

Where b_{ak} is the Tafel slope for anodic polarisation of wire k . The cathodic reaction current can be written as:

$$I_{kc} = I_k \exp [-2.3 (E_{sys} - E_k) / b_{ck}] \quad (2.3)$$

Where b_{ck} is the Tafel slope for cathodic polarisation of wire k . Substituting equation 2.1, 2.2, and 2.3 gives:

$$I_{ka} = I_{gk} / \{1 - \exp [-(2.3/b_{ak} + 2.3/b_{ck})(E_{sys} - E_k)]\} \quad (2.4)$$

If the open-circuit potentials of wires in a WBE are very different from the potential of the whole system (i.e., the wires are under large polarisation), equation 2.4 can be simplified:

$$I_{ka} = I_{gk} \quad (2.5)$$

The criterion that permits the simplification of Equation 2.4 to 2.5 could be that the difference between the open-circuit potential of a wire and the potential of the whole system is >100 mV, an analogue to the validity condition of the Tafel equation [Tan 1998]. Localised corrosion current on all locations of the WBE can be estimated using equation 2.2, 2.4, or 2.5.

In this way, the galvanic current distribution, the potential distribution, as well as the corrosion rate distribution over the WBE surface can be mapped. Distributions of galvanic current, potential and localised corrosion rates over the WBE surface can then be shown with a 3-dimensional spatial plot or a contour map. Typical maps of WBE measurement are shown in Figure 2.15.

Figure 2.15 Typical results of WBE measurement [Source: Tan *et al.* 2001b]

On the WBE maps, the regions with positive galvanic current densities indicate the anodic sites, while regions with negative values denote cathodic sites. The larger the positive galvanic current density, the more severe the localised corrosion is.

A further development on WBE technique was made by combining this technique with another technique, namely electrochemical noise resistance measurements (R_n). The obtained electrochemical data were used to determine corrosion rates and their distribution and then to calculate accumulate corrosion depths [Tan *et al.* 2000].

Based on the assumption of uniformity of each wire surface, I_k in equation 2.2 can be expressed in Stern-Geary equation:

$$I_k = \frac{b_{ak}b_{ck}}{2.303(b_{ak} + b_{ck})} \cdot \frac{1}{R_{pk}} \quad (2.6)$$

Where R_{pk} is the polarisation resistance of wire k, which can be measured using traditional electrochemical techniques such as the linear polarisation method. It has been reported that electrochemical noise resistance (R_n) was similar (or equivalent) to polarisation resistance (R_p) [Skerry and Eden 1991]. Thus the corrosion current of wire k can be calculated as,

$$I_k = \frac{b_{ak}b_{ck}}{2.303(b_{ak} + b_{ck})} \cdot \frac{1}{R_{nk}} \quad (2.7)$$

Combination of equation 2.2 and equation 2.7 gives

$$I_{ka} = \frac{b_{ak}b_{ck}}{2.303(b_{ak} + b_{ck})} \cdot \frac{1}{R_{nk}} \cdot \exp \left\{ \frac{2.303(E_{sys} - E_k)}{b_{ak}} \right\} \quad (2.8)$$

Then the instantaneous corrosion rate of wire k, CR_k (in a unit of mm/y), can be calculated with I_{ka} as

$$CR_k = \frac{10 \times 365 \times 24 \times 3600 E_w b_{ak} b_{ck}}{2.303 d F (b_{ak} + b_{ck})} \cdot \frac{1}{R_{nk}} \cdot \exp \left\{ \frac{2.303(E_{sys} - E_k)}{b_{ak}} \right\} \quad (2.9)$$

Where E_w is the equivalent weight of the electrode material, d is the density of electrode material; F is the Faraday constant (96485). Based on equation 2.9, localised corrosion rates at all locations of the WBE can be calculated. In this way, the corrosion rate and its distribution over the WBE can be mapped. The WBE in conjunction with electrochemical noise method has been successfully applied to study several electrochemical processes [Tan 2000; Tan *et al.* 2001a and b]. The

correlation between the calculated and observed corrosion depth maps, as shown in Figure 2.16, was good.

Figure 2.16 Calculated and observed corrosion depth maps over a mild steel WBE

[Source: Tan *et al.* 2000]

Crevice corrosion and waterline corrosion have been studied using a steel WBE in carbon dioxide and oxygen environments [Tan *et al.* 2001b and c]. The accumulated corrosion depth distribution map obtained using WBE presented good correlation with the corrosion depths determined by microscopic observation. The measured instantaneous kinetics of crevice corrosion was found to be quantitatively comparable with microscopic observation of the corroded electrode surface. This technique has also been successfully applied in studying the CO₂ corrosion [Tan *et al.* 2001b], distribution of cathodic protection currents over a protected surface [Tan

1999]. Similar corrosion patterns were experimentally observed over a WBE and a large area one-piece electrode when both electrodes were exposed to an identical environment [Tan 1998; 1999].

In conclusion, the WBE has been experimentally proven to be a convenient new tool in monitoring localised corrosion processes and patterns, as it can relate the anodic and cathodic processes to the anodic and cathodic regions

CHAPTER 3

Experimental

3.1 Materials and Electrode Preparation

Commercial pure aluminium AA1100 and high strength aluminium alloy AA2424-T3 have been utilized in this project. Commercial pure aluminium AA1100 plate with a thickness of about 5 mm and AA1100 wire with a diameter of about 0.12 mm, were provided by Sin Hong Huat Aluminium Pte. Ltd., Singapore. Its composition is listed in Table 3.1.

Table 3.1 Composition limits of AA1100

Elements	<i>Si</i>	<i>Fe</i>	<i>Cu</i>	<i>Mn</i>	<i>Zn</i>	<i>Al</i>
Wt %	<1.0 (Si + Fe)		0.05-0.20	0.05	0.10	99.00

Aluminium alloy AA2024-T3 was supplied by Sin Hong Huat Aluminium Pte. Ltd., Singapore. Its composition is listed in Table 3.2.

Table 3.2 Composition of AA2024-T3

Elements	<i>Al</i>	<i>Mg</i>	<i>Cu</i>	<i>Mn</i>	<i>Fe</i>	<i>Zn</i>	<i>Ni</i>	<i>Si</i>
Wt %	93.75	1.34	3.78	0.7	0.2	0.17	0.025	< 0.024
<i>Std. Deviation</i>	0.04801	0.02826	0.06873	0.03002	0.01156	0.00772	0.00202	
Elements	<i>Cr</i>	<i>Sn</i>	<i>Pb</i>	<i>V</i>	<i>Ti</i>	<i>Ca</i>	<i>Be</i>	
Wt %	0.02	0.029	< 0.013	0.0048	< 0.011	< 0.0015	< 0.0004	
<i>Std. Deviation</i>	0.00112	0.00055	0.00055	0.00007	0.00037	0.00003	0	

Materials used for the fabrication of WBE specimen was a commercial aluminium alloy AA2024 plate with a thickness of 1.2 cm in the as-received T3 temper state, namely the so called AA2024-T3 plate. Where T stands for thermally treated, and T3 means solution heat treated then cold worked (usually the annealing temperature is 413 °C, and the solution temperature is 256 °C). All the results of AA2024-T3 in this thesis were obtained from the AA2024-T3 material in the as-received state (with no artificial heat treatment). The microstructure of the AA2024-T3 plate was illustrated in Figure 3.1. The AA2024-T3 plate has three different orientations, i.e. longitudinal (L), long transverse (LT) and short transverse (ST). Working surface of the WBE specimen was the longitudinal (L) section. High magnification of the microstructure of L section was shown in Figure 3.1 (b). In order to compare the results obtained from the WBE specimen and the one-piece electrode, working surface of the one-piece electrodes for SEM observation were also prepared on the longitudinal section. Wires for the fabrication of WBE specimen were prepared by cutting the AA2024-T3 plate using a precise cutting machine. Coolant was used during the whole period of cutting process. The cutting surface was then wet polished up to 1000 grit SiC paper. Sampling locations were shown in Figure 3.2.

Figure 3.1 Microstructure of three orthogonal sections of the 12 mm thick AA2024-T3 plate used in the experiment (as received).

Figure 3.2 Schematic diagram shows the sampling locations and the testing surfaces (orientations) of the one-piece electrode and the WBE.

Specimen Preparation

One-piece Electrode -- One-piece electrodes were prepared by cutting aluminium sheets (AA1100 or AA2024-T3) into 1.1cm × 1.1cm coupons. The coupons were mounted with epoxy, as shown in Figure 3.3, and polished up to 1000-grit SiC paper, rinsed with deionised water, degreased with ethanol, and dried in the air.

Figure 3.3 (a) side view of electrode for polarisation experiment (b) side view of electrode for SEM observation, and (c) top view of the electrodes in (a) and (b)

Wire Beam Electrode (WBE) -- One hundred AA1100 wires (cut from the as received AA1100 wire with a length of about 30 cm) coated with epoxy were mounted together in 10×10 array using epoxy resin. The epoxy and hardener used for specimen mounting were provided by Chemicrete Enterprises Pte. Ltd., Singapore. The epoxy resin for specimen preparation was prepared by mixing 10 parts epoxy with 4 parts hardener at room temperature. Every ten pre-coated wires (as one group) were put together as close as possible. The ten wires were then coated with another thin layer of epoxy resin at desired length and were pressed using a heavy stuff to get a flat surface, as shown in Figure 3.4 (a). Following the same procedure, the one hundred wires were prepared into ten groups. The ten groups were then bundled together in an arrangement of ten layers (a thin layer of epoxy resin was applied between every two adjacent layers, as shown in Figure 3.4 (b)). Finally, these one hundred wires were connected with data cables.

Figure 3.4 Preparation procedures for WBE specimen

The work surface of the WBE fabricated from AA1100 is shown in Figure 3.5 (a). In order to situate the specimen in the SRET tank precisely, the WBE was prepared

with a shape as shown in Figure 3.5 (b). Each wire had a surface area of about 0.01166 cm^2 ; the whole area of the work surface of WBE specimen was about $1.5 \text{ cm} \times 1.5 \text{ cm}$ (total metallic area was about 1.166 cm^2). The AA2024-T3 WBE was made from one hundred AA2024-T3 wires (sampling locations and working surface were illustrated in Figure 3.2). It had a total working metallic area of about 1.44 cm^2 . Its working surface is shown in Figure 3.5 (c). Before each experiment, the WBE specimen was polished using 180, 320, 600, and 1000-grit SiC paper, rinsed with deionised water, degreased with ethanol, and dried in the air.

Figure 3.5 (a) and (b) WBE made from AA1100, (c) AA2024-T3 WBE

Electrolytes Preparation

Chemicals used in the experiments were reagent-grade, which are listed in Table 3.3. Deionised water was used for the preparation of electrolyte solutions.

Table 3.3 Chemicals used in the project

Chemical	Provided by
Sodium chloride	Sino Chemical Co. Pte. Ltd., Singapore
Cupric sulphate	Sino Chemical Co. Pte. Ltd., Singapore
Potassium dichromate	Sino Chemical Co. Pte. Ltd., Singapore
Cerium chloride	Sino Chemical Co. Pte. Ltd., Singapore
Lanthanum chloride	Sino Chemical Co. Pte. Ltd., Singapore
Sodium molybdate	Sino Chemical Co. Pte. Ltd., Singapore

3.2 Experimental Setup

Figure 3.6 shows schematic experimental setups for investigating localised corrosion from both the metallic and electrolyte phases of a corroding metal surface. The WBE method is used to map current and potential distributions in the metallic phase, and the SRET is used to map current or potential distribution in the electrolytic phase. In this project, the studies of aluminium corrosion and its inhibition were mainly carried out either under free corrosion conditions, as shown in Figure 3.6 (a), or under anodic polarisation, as shown in Figure 3.6 (b).

(a) Studying free corrosion

(b) Studying corrosion under anodic polarisation

Figure 3.6 Schematic setup of a WBE in combination with SRET measurements (a) studying free corrosion (b) studying corrosion under anodic polarisation condition

The SRET system used in the experiments consisted of a personal computer, a video telescope and a SP100 SRET (EG&G Company, USA), as shown in Figure 3.7.

Figure 3.7 Photograph of the setup of SRET measurement

Typical layout of the SP 100 SRET is shown in Figure 3.8. It mainly consisted of the following components:

A scanning head: The probe arrangement utilised in the SRET consists of two platinum tips, of which their diameter is in the order of one to five micrometers. These tips are housed within a single unit in close lateral proximity, but spaced vertically from each other by a few millimetres, as shown in Figure 3.8. The probe moves horizontally in order to build up two dimensionally resolved data. The work surface (specimen surface) on which the SP100 scanning head was to be sited should be as level as possible; this was checked with a spirit level. The distance between the work surface and the probe tip was kept constant during the experiment. The best resolution and sensitivity were obtained if the distance located in the range of less than 100 μm , as recommended by the manufacture. By scanning the probe

(scanning head), potential variations caused by the corrosion current flowing from anodes to cathodes within the electrolyte can be measured over the specimen surface.

Figure 3.8 Typical layout of the SP 100 SRET used in the project

[Source: SP100 SRET manual, EG & G Instruments]

- **An electrolyte tank:** for containing testing solution and positioning testing samples
- **A control electronics unit:** for controlling the movement of scanning head and collecting the electronics data resulted from the studying system

Movements of the scanning probe in x and y directions are approximately 100 mm whilst vertical movement (z) is about 35 mm. Internal unity gain of

the system can go up to 5000. Scanning speeds is continuously defined from 1000 μm to 25 mm/second. There are two scanning-modes that can be chosen for a scanning. One is *Line Scan* and the other is *Area Map Scan*, which is widely used in this project. The system allows the operator to specify a number (8, 16, 32, 64, 128, 256, or 512 samples per line), which will constitute the number of channels in the x-axis that the data will be recorded into. For very fast, low resolution scans, a lower number can be specified. For high resolution, but slower scan times, a higher number can be selected.

The WBE used in this project mainly consisted of an AutoSwitch v2 (custom made), a computer, and a measurement instrument -- AutoAC, namely GillAC (ACM instruments, England), as shown in Figure 3.9.

Figure 3.9 Photograph of the setup for WBE measurement

- **AutoSwitch:** A computer controlled automatic switch is used to connect the measurement instrument (AutoAC) with one or more chosen wires.
- **AutoAC:** It can function as a voltmeter to record corrosion potential of each wire, as shown in Figure 3.10 (a), and also function as an auto zero resistance ammeter to measure current flowing between each wire and the remaining wires of the whole wire bundle, as shown in Figure 3.10 (b). AutoAC

enables current and voltage to be measured accurately and to be recorded automatically from a WBE surface through pre-programmed systematic measurements. The corrosion potential distribution is obtained by sequentially measuring the open circuit potential of each wire against the reference electrode (SCE) using the AutoAC and AutoSwitch. The galvanic currents flowing between each individual wire and the wire beam system are measured by sequentially inserting the AutoAC between a chosen wire terminal and all other terminals shorted together using the AutoSwitch. Current or potential values measured from each wire of WBE (I_k and E_k , $k = 1 - 100$) are plotted using professional software MathCAD 2000, to produce a WBE galvanic current distribution or a WBE potential distribution map.

Figure 3.10 Schematic illustrations of the measurement of potential and galvanic current of each wire of a WBE specimen

Polarisation Measurements

Polarisation techniques including cyclic potentiodynamic polarisation were also used to study aluminium corrosion and its prevention. The setup of polarisation experiment is schematically illustrated in Figure 3.11. It consists of a computer, an AutoAC, a salt bridge, an auxiliary electrode, a reference electrode (SCE), an electrochemical cell, and a single piece electrode. The procedure of cyclic potentiodynamic polarisation was generally in accordance with the standard ASTM Designation G61.

Figure 3.11 Arrangement of the polarisation experiment

Before initiating polarisation, the specimen was immersed in the electrolyte for 1 hour. To run the cyclic potentiodynamic polarisation, the pre-programmed 'Cyclic Sweep' mode was selected. The potential scan began at the corrosion potential (open circuit potential) and scanned in the more noble direction at a scan rate of 10 mV/min. The reverse scanning potential was usually set at about 500 mV higher than the open circuit potential. At this potential, scanning direction was reversed (toward more active potentials). The onset of localized corrosion was usually

marked by a sharp increase of the anodic current at potentials below the oxygen-evolution potential. This experiment was always carried out at air-conditioned room temperature ($\sim 25\text{ }^{\circ}\text{C}$)

Microscopic and Surface Analysis

After each experiment, specimen surface was examined by visual and microscopic examination. The observation was mainly carried out using two models of optical microscopes, i.e. Nikon Epiphot 2000 (magnification from $0.63\times$ to $4\times$) and Nikon Epiphot 200 (magnification from $50\times$ to $1000\times$).

Corroded specimen was also examined using SEM and EDS. SEM observation was carried out using JSM-5410 (JEOL, Japan) equipped with EDS (OXFORD 6993, England), and JSM-6360 equipped with EDS (JEOL EX-54175JMU). SEM was used to study changes of the topography of specimens before and after exposure to electrolyte, while EDS used to provide information on elemental changes and characterisation of various second phase particles in aluminium alloys. In this project, SEM and EDS were employed to obtain supporting information regarding localised corrosion of AA2024-T3 in sodium chloride solution with or without inhibitors. Specimens for SEM examination were generally prepared by immersing AA2024-T3 in certain electrolyte for various durations of exposure, e.g. 1 hr, 2 hrs, 4 hrs, 8 hrs, 12 hrs, 24 hrs, 36 hrs, and 48 hrs.

3.3 Experimental Procedures

Studies of aluminium corrosion and its inhibition using WBE and SRET were carried out under free corrosion conditions or under anodic polarisation conditions.

- Procedure for experiments under free corrosion conditions:
 - 1) The WBE was positioned in the SRET electrolyte tank. Its surface was adjusted using a spirit level until it was level.
 - 2) Electrolyte was poured into the tank.
 - 3) The probe was then positioned over the area of the WBE. The x and y position was determined by eye. The distance between the probe and the work surface of the specimen (z direction) was adjusted to a certain value (usually $\leq 100 \mu\text{m}$), which was carried out using a computer with the aid of a telescope.
 - 4) The gain of SRET system was set at $2000\times$ and the X- velocity of scan was set at $20000\mu\text{m}/\text{sec}$.
 - 5) The WBE was then connected to the Autoswitch using data cables.
 - 6) WBE and SRET measurements were carried out at certain time intervals. For the AA1100 WBE specimen, each reading of the WBE measurement would take about 15 minutes, and SRET reading would take about 10 minutes. For AA2024-T3 WBE specimen, each reading of the WBE measurement would also take about 15 minutes, however, the SRET reading would take about 11 minutes. Generally, readings were taken in the sequence of:
WBE $\rightarrow$ SRET $\rightarrow$ WBE $\rightarrow$ SRET ...
- Procedure for experiments under anodic polarisation:
 - 1) Steps 1 to 5 were the same as the above experimental procedure.
 - 2) An auxiliary electrode and a reference electrode were placed in the electrolyte tank and connected to an AutoAC.
 - 3) Open circuit potential (OCP) was measured using the AutoAC. When OCP became relatively stable, readings of WBE and SRET were taken under free corrosion condition.
 - 4) A D.C offset potential at pre-determined value, which can be adjusted in

the pre-programmed 'Potentiostatic', was applied to the WBE. For instance, a constant +50 mV offset potential can be applied above the OCP, and the WBE was thus under an anodic polarisation condition in the corrosive media.

- 5) Readings of WBE and SRET were then taken.
- 6) After WBE and SRET measurements were completed, the offset potential was then changed to other values, or the offset potential was removed. SRET and WBE measurement were taken to detect the changes of corrosion activity over the WBE surface.

CHAPTER 4

Development of a New Technique Based on the Combined Use of WBE and SRET -- Initial Exploratory Work

4.1 Exploratory Work using Mild Steel WBE

Determination of ionic currents in the electrolytic phase and electronic currents in the metallic phase, generated from electrochemical corrosion cells, as well as their distributions over the metal/solution interface is useful not only for understanding corrosion mechanism, but also for determining corrosion kinetics and for predicting corrosion patterns.

A new method that could be utilised to achieve this objective is to use the WBE method in conjunction with the SRET for simultaneous measurement of ionic and electronic currents from both the metallic and electrolytic phases of a corroding metal surface. A schematic diagram showing the principle of this new method is illustrated in Figure 4.1. An ACM instrument AutoAC (functioning as AutoZRA) is employed to measure galvanic current flowing between each individual wire and the remaining wires (coupled together) in a WBE. Corrosion potential of each individual wire against a reference electrode can be also measured using this AutoAC (functioning as a voltmeter). The galvanic corrosion current and potential of all the individual wires of a WBE (such as wire k in Figure 4.1) can be measured by the AutoAC in sequence by means of an automatic switch. Meanwhile, in the electrolyte phase, the potential variations caused by the corrosion current flowing from anodes to cathodes can be detected using the SRET measurement by scanning the probe over the specimen surface.

For instance, when corrosion occurs at wire k (anode), I_{gk} can be measured using the AutoAC, and a positive value is recorded. While in the electrolytic phase, the SRET

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can detect the potential distribution caused by ionic currents in the electrolyte. Hence the combined usage of WBE and SRET could provide unique capabilities in studying localised corrosion.

(a) Schematic diagram

(b) Enlarged

Figure 4.1 Schematic diagrams showing the principle of the combined usage of WBE and SRET for measuring galvanic corrosion current and potential distribution (WBE) through the metallic phase, and potential variation (SRET) via electrolytic phase.

Before starting to investigate aluminium localised corrosion and its inhibition, exploratory experiments have been carried out to study classical steel corrosion in Evans solution. The objective was to evaluate the applicability, sensitivity, advantages and/or limitations of this unique technique as a tool of investigating electrochemical corrosion processes.

A novel experimental setup is schematically illustrated in Figure 4.2. The WBE specimen was fabricated from 100 mild steel wires (0.18 cm in diameter) embedded in epoxy resin. Each wire in the WBE acts both as a mini-electrode sensor and also as a corrosion substrate. The total working area (the area occupied by the wire beam) was approximately 3.24 cm² and the metallic area is approximately 2.54 cm². Solution used in the experiment was the Evans solution (0.017 M sodium chloride and 0.008 M sodium carbonate), in which mild steel would undergo a classical localised corrosion leading to distinct separation of the anodic and cathodic areas on steel surface [Evans 1960].

Figure 4.2 Schematic experimental set-up of WBE in combination with SRET

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Typical results of WBE and SRET measurements from a mild steel WBE, in Evans solution (pH 10.63) is shown in Figure 4.3.

Figure 4.3 (a) and (b) The WBE galvanic current density (mA/cm^2) and potential (V vs. SCE) distribution maps, and (c) SRET map, measured from a mild steel WBE surface after about 30 hours immersion in the Evans solution, together with (d) photo showing the corroded WBE surface after 30 hours immersion.

The WBE current and potential maps clearly correlate with each other, as shown in Figures 4.3 (a) and (b). In particular, the anodic sites in the WBE maps (i.e. areas with positive current and more negative potential values) correlate well with the main anodic sites (with negative voltage values) in the SRET map, as shown in Figure 4.3 (c). In this classic localised corrosion system, the main anodic sites remained almost unchanged during the whole period of experiment. This is evident that the corrosion pattern shown in the photo of the electrode surface after 30 hours of corrosion exposure (Figure 4.3 (d)) correlates well with WBE and SRET maps. The typical features in Figure 4.3 are reproducible, although the exact locations of corrosion anodes and cathodes did not remain the same in repeated experiments.

However, Figures 4.3 (a), (b) and (c) show that the cathodic sites detected by SRET are different from those by WBE. One finding from these experiments was that in Figure 4.3 (c), major cathodic zones located near the right side of the major anodic zones, while both WBE maps indicate a large cathodic zone over the whole WBE surface. This is a phenomenon that has been observed repeatedly in our other experiments, and it is believed to be an artefact which is produced during the SRET measurement. Possibly, such artefact may be due to the following two reasons:

i) Interference of SRET scanning on electrochemical corrosion processes -- During SRET measurement, the scanning tip moved from left to right direction (as indicated in Figure 4.3 c). This movement is expected to stir the solution and thus to enhance mass transportation over the electrode surface and to interfere the steady-state anodic and cathodic reactions. As a result, at the time of scanning, cathodic reaction near the right side of the anodic zone was significantly accelerated, and thus large cathodic currents were detected by SERT instrument. For this reason, the cathodic site detected by SRET is believed to be incorrect. The influence caused by the movement of the scanning probe on the corrosion process was verified by an experiment by scanning the SRET probe in normal and reverse directions. As shown in Figures 4.4 (b) and (d), it is clear that the location of cathodic area detected by the SRET may be dependent on the scanning direction of the probe. This problem should be considered a limitation of the SRET method and deserves further study.

Figure 4.4 (a) Schematic of scanning direction over the Mild steel WBE surface, (b) SRET map obtained by scanning in normal direction, (c) galvanic current distribution map, and (d) SRET map by scanning in reverse direction

ii) Interference of the scanning speed of the probe -- When the probe is scanning over the sample surface in a very high speed, it may influence the SRET potential data if the probe's response is slow. The time constant is the term for determining the probe's response time, which determines how rapidly the probe output signal changes for a sudden change in the probe input signal. If the probe input signal changes suddenly, the time constant expresses the time it takes for the probe output signal to reach 63.2% of its final value. The time constant of SRET is about 0.1

second. Since the SRET technique correctly detected the anode locations, it suggests that the time constant and scanning speed of SRET did not significantly affect the measurement.

Further experiments have been carried out to test the ability of this WBE and SRET method in monitoring the changes in corrosion behaviour. The pH of the Evans solution was adjusted from originally 10.63 to lower values by gradually adding HCl acid. Figures 4.5 – 4.9 show typical WBE and SRET maps measured at the various stages of solution pH adjustments. When the pH of solution was just adjusted from 10.63 (Figure 4.5) to 10.03, both WBE (Figure 4.6 (a)) and SRET (Figure 4.6 (b)) measurements detected one major anode. The anodic current density at the anodic site was high (the maximum value was 2.06 mA/cm^2). With the extension of exposure, the number of anodic sites increased considerably and the anodic current density decreased, suggesting that corrosion became more general and less concentrated, Figures 4.6 (c) and (d).

Figure 4.5 (a) WBE galvanic current map and (b) SRET map obtained from a mild steel WBE in the Evans solution with pH of 10.63 for 4 hrs

Figure 4.6 WBE current distribution maps and SRET maps obtained from a mild steel WBE after exposed to the Evans solution with a pH of 10.03 for (a) and (b) 10 mins, and (c) and (d) 2 hrs

When solution pH decreased further to 8.87, more wires in the WBE became anodes and the maximum galvanic current density kept decreasing. Obviously the corrosion pattern changed from localised to general, as shown in Figure 4.7 (a) and (b). The correlation between WBE, SRET, and visual observation was obvious, although the WBE map appeared to show more details on the local anodic and cathodic sites.

Figure 4.7 (a) WBE current distribution map, and (b) SRET map of a Mild steel WBE in the Evans solution with a pH of 8.87

With the pH decreased further to 6.93, as shown in Figure 4.8, corrosion pattern became more and more general. Higher cathodic currents were recorded along the edges of the WBE with the magnitude decreasing in a contour-like manner towards the centre of the WBE surface. This pattern suggests an oxygen concentration-controlled general corrosion behaviour due to higher oxygen concentrations at corners and edges where oxygen supply was more sufficient through two- or three-dimensional diffusion. In this case, oxygen concentration distribution was a dominant factor determining the corrosion pattern. With corrosion pattern became more general, the SRET and WBE maps became less correlated with each other. This is understandable since the separation of the anodic and cathodic areas on steel surface became less distinctive when corrosion became more general.

Figure 4.8 The WBE galvanic current distribution maps and SRET maps measured from a mild steel WBE surface after (a) and (b) 1 hour, and (c) and (d) 24 hours immersion in the Evans solution with a pH of 6.93

When the solution pH decreased further to 1.98, major changes in corrosion pattern occurred – the distribution of anodic and cathodic sites became random, as shown in Figure 4.9, which may indicate a corrosion mechanism change, i.e. the dominating cathodic reaction changed from oxygen reduction to hydrogen evolution. In this case, corrosion was not under diffusion control due to sufficient supply of hydrogen ions. The hydrogen evolution can become very fast and thus can become the predominant cathodic reaction. In such system, the anodic and cathodic sites became not distinctly separated, and thus correlation between WBE and SRET maps was largely

lost. The WBE map still appears to reflect corrosion activities over the electrode surface.

Figure 4.9 (a) WBE current distribution map, and (b) SRET map of a Mild steel WBE in Evans solution with a pH of 1.98

The experiments carried out in the Evans solution with varying pH values indicates that the combined WBE and SRET method is useful in detecting the change of corrosion processes and patterns.

Another experiment has been carried out to evaluate the behaviour of the new method when it was applied to a coated corrosion system. A mild steel WBE was sprayed with a layer of WD-40 oil (WD-40 Company, USA) film after being polished using 1000 grit SiC papers and cleaned with deionised water and ethanol. The coated WBE surface is dried in air for two days before being exposed to the Evans solution in a similar arrangement as described in Figure 4.2.

At the beginning of the exposure, as shown in Figure 4.10 (a), there were 37 wires that behaved as anodes and the galvanic current values detected by WBE method were very small (maximum anodic current was 0.068 mA/cm²). These anodic sites were believed to be the weakness sites in the WD-40 oil layer, which could be attributed to the electrochemical inhomogeneity of organic coatings [Tan 1991; Wu *et al.* 1996]. It is interesting to note that the locations of major anodic sites remained

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almost unchanged, but the number of anodic sites decreased considerably with the extension of exposure. The maximum galvanic current increased steadily from 0.068 mA/cm^2 to 0.481 mA/cm^2 during 20 hours of exposure, suggesting that corrosion became more and more localised. This result is surprising since extended exposure to corrosion environment is expected to cause continued degradation of the oil film and thus more anodic sites. The mechanism of this phenomenon is unknown and requires further detailed investigation.

Figure 4.10 The WBE galvanic current distribution maps and SRET maps measured from a coated mild steel WBE surface after (a) and (b) 1 hr, and (c) and (d) 20 hrs immersion in the Evans solution

This experiment confirms that the combination of WBE and SRET is a useful tool in studying localised corrosion through both the metallic and electrolytic phases. Detailed heterogeneous electrochemical parameters of localised corrosion can be easily obtained using this experiment method.

4.2 Localised Corrosion Intensity Index

Current density data in WBE maps, such as the galvanic current map shown in Figure 4.5 (a), can be registered in a data table, as shown in Table 4.1. The maximum anodic current density (i_{max}), which has the largest positive current density value, and the number of anodes (N_a), which is the number of wires that have a positive current density, can be obtained from Table 4.1. For instance, i_{max} in Table 4.1 is 0.2784 mA/cm², and N_a is 5.

Table 4.1 Data table from WBE map of Figure 4.5 (a) (galvanic current density: mA/cm²)

-0.006	-0.014	-0.011	-0.022	-0.008	-0.001	-0.008	<i>0.0011</i>	-0.009	-0.016
<i>0.2199</i>	<i>0.2784</i>	-0.005	-0.013	-0.003	-0.01	<i>0.003</i>	-0.003	-6E-05	-0.012
-0.004	<i>0.0566</i>	-0.006	-8E-04	-9E-04	-0.006	-0.007	-0.007	-0.007	-0.007
-8E-04	-0.004	-0.006	-0.006	-0.006	-0.006	-0.005	-0.006	-0.006	-8E-04
-6E-04	-0.002	-0.006	-0.005	-0.006	-0.005	-0.006	-0.006	-0.006	-0.008
-0.004	-0.004	-0.005	-0.005	-0.006	-0.006	-0.005	-0.006	-0.007	-0.008
-0.009	-0.006	-0.006	-0.006	-0.006	-0.007	-0.005	-0.006	-0.006	-0.007
-0.008	-0.008	-0.014	-0.006	-0.006	-0.006	-0.007	-6E-04	-0.006	-0.007
-0.008	-0.007	-0.007	-0.006	-0.009	-0.007	-0.006	-0.007	-0.008	-0.007
-0.008	-0.013	-0.011	-0.012	-0.008	-0.011	-0.008	-0.007	-0.006	-0.008

The total anodic current density (i_{tot}) is the sum of all the measured anodic current densities. It can be calculated by adding all the current densities with positive values in the data table. For instance, in Table 4.1, i_{tot} can be obtained by adding all the five positive anodic current values (bold and italic font) shown in the table using the following equation:

$$i_{tot} = \sum_{n=1}^{N_a} i_n$$

Where i_n is the measured anodic current density from an individual wire, which has a positive value ($i_n > 0$). Thus, i_{tot} can be obtained as

$$i_{tot} = 0.2199 + 0.2784 + 0.0566 + 0.0011 + 0.003 = 0.5579 \text{ mA/cm}^2$$

The maximum anodic current density can be used to describe the extent of localised corrosion attack – the rate of anodic dissolution of the most active anode. The total anodic current density can be used to describe overall corrosion of the specimen. Obviously, the larger the total anodic current density, the more severe the total corrosion. Meanwhile, the degree of localisation of corrosion can be expressed by the reciprocal of the number of anodes ($1/N_a$). Obviously, for a WBE consisting of 100 wires, the larger the $1/N_a$, the more localised the corrosion, as shown in Figure 4.11.

Figure 4.11 (a) Most localised, (b) localised, and (d) less localised corrosion

The ratio of the maximum and total anodic current density, i_{max}/i_{tot} , can be used to describe the non-uniformity of anodic current distribution (how localised the anodic current is distributed). Figure 4.12 shows two typical cases, which are used as examples to illustrate the parameter of i_{max}/i_{tot} . In these two cases, total anodic currents are assumed to be equal. For the case shown in Figure 4.12 (a), there is only one major anode, which has a very large current density. Thus,

$$i_{max} \approx i_{tot} \Rightarrow i_{max} / i_{tot} \approx 1$$

In the situation shown in Figure 4.12 (b), there are 5 major anodes. Thus,

$$5i_{max} \approx i_{tot} \Rightarrow i_{max} / i_{tot} \approx 0.2$$

It can be seen that the larger the i_{max}/i_{tot} ratio, the more localised the anodic currents are distributed.

Figure 4.12 (a) More localised corrosion attack – mainly concentrated at one site (b)
Less localised attack – mainly concentrated at five sites

In order to describe the degree of localisation of corrosion, here we introduce a new parameter namely the localised corrosion intensity index (*LCII*). *LCII* can be defined by the combination of $1/N_a$ and i_{max} / i_{tot} . It can be written as,

$$LCII = \left(\frac{i_{max}}{i_{tot}} \right) \bullet \left(\frac{1}{N_a^{3/2}} \right) \quad (4.1)$$

Where 3/2 is a weight factor. In this thesis, the determination of a corrosion system whether was localised or general was mainly dependent on the “number of anodes”,

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i.e. the more the anodes, the more general the corrosion system. If two corrosion systems have the same anodes, then current distribution among anodes become important. Current distribution (i_{max} / i_{tot}) is used to indicate current distribution of the most major anode over all anodes. If anodic current is more concentrated on small number of anodes, then the i_{max} / i_{tot} should be large and more severe the localised corrosion. However, we consider that the “number of anodes” to be a more important parameter in describing a corrosion system than anodic current distribution indicated by i_{max} / i_{tot} . Thus, a weight factor (3/2) was introduced into the formula of “Localised Corrosion Intensity Index” to illustrate the more important factor, “number of anodes”.

Obviously, the larger the **LCII**, the more localised the corrosion. This localised corrosion intensity index can be used to quantify the degree of localised corrosion.

Based on the equation 4.1, localised corrosion index (**LCII**) of the mild steel in the Evans solution with various pH values can be calculated. The change of localised corrosion intensity index as a function of the pH of the Evans solution is shown in Figure 4.13 (a). Figure 4.13 (b) shows the same result as a function of exposure time, corresponding to WBE maps in Figures 4.5 - 4.9.

(a)

Figure 4.13 Change of localised corrosion intensity index of mild steel as a function of the pH of the Evans solution

Based on the mild steel results and analysis, it could be seen that electrochemical parameters regarding non-uniform corrosion processes can be conveniently obtained using WBE in conjunction with SRET method. The advantages of the combined usage of WBE and SRET method include:

- It could provide unique information regarding corrosion process, kinetics, pattern, and mechanism.
- Electrochemical parameters such as localised corrosion intensity index, number of anodes, maximum and total anodic current densities could be obtained. They could be used to quantify and study localised corrosion.
- When the correlation between the WBE and SRET results is established, SRET can then be applied to study localised corrosion independently using one-piece electrode. One-piece electrode is more convenient to prepare than the WBE.

CHAPTER 5

Results and Discussion I: Studies on Aluminium Corrosion Behaviour and Mechanism

For the first time the WBE has been applied to study AA1100 and AA2024-T3 corrosion and its inhibition in conjunction with SRET. Traditional techniques, such as SEM observation and polarisation measurements, have also been used to obtain additional information from the corrosion systems being investigated.

5.1 AA1100 Corrosion in Sodium Chloride Solutions

AA1100 has controlled unalloyed composition and is used primarily in the electrical and chemical industries. Corrosion resistance of AA1100 is very high, although under some conditions, it decreases slightly with increasing alloy content [Davis 1999]. In the oxide stable range of pH 4 to 9, it is subject only to water staining of the surface and to localised pitting corrosion [Lifka 1996]. In order to achieve better understanding of its corrosion behaviour and mechanism, AA1100 has been studied in neutral sodium chloride solution under free corrosion and anodic polarisation conditions using WBE in conjunction with SRET measurements.

5.1.1 AA1100 Corrosion under Free Corrosion Conditions

Figure 5.1 shows typical WBE galvanic current distribution maps and a SRET map measured from an AA1100 WBE surface exposed to 0.5 M sodium chloride solution.

From WBE current maps in Figure 5.1 (a) and (b), it could be seen that corrosion was taking place with anodic sites distributing over the WBE surface in a random manner at the beginning of corrosion exposure. The anodic current values were low with the maximum anodic current density in the range of $\mu\text{A}/\text{cm}^2$. At later stages of exposure, as shown in Figure 5.1 (c), (d) and (e), corrosion became more localised, and the maximum anodic current density also increased to $0.028 \text{ mA}/\text{cm}^2$.

In this corrosion system, the SRET map obtained was ‘empty’, as shown in Figure 5.1(f). It may be because that 0.5 M sodium chloride solution had a high conductivity, and that the corrosion current density was too small. SRET was not able to detect such small currents in a high conductivity solution, and thus an ‘empty’ map was obtained. The sensitivity of SRET is dependent heavily upon the value of the current in the electrolyte, the conductivity of the electrolyte, the distance between the probe tip and the specimen surface, and also the distribution of anodes and cathodes on the specimen surface. This result indicates that the SRET has a limitation in detecting this type of slow aluminium corrosion that produces only small currents flowing between local anodes and cathodes.

Figure 5.1 WBE galvanic current distribution maps obtained after (a) 30 mins, (b) 4 hrs, (c) 12 hrs, (d) 24 hrs, and (e) 48 hrs and (f) SRET map obtained after 30 mins immersion in 0.5 M NaCl solution

Values of maximum anodic current density ($i_{\max}$) and total anodic current density (i_{tot}) can be obtained from maps in Figure 5.1, using methods described in Section 3.4. The changes of $i_{\max}$ and i_{tot} with immersion time are shown in Figure 5.2.

From Figure 5.2, it can be seen that during 48 hours immersion in 0.5 M sodium chloride solution, both the maximum and total anodic current densities increased with immersion time and became relatively stabilised after 10 to 20 hours.

The change of number of anodes (N_a) and localised corrosion intensity index ($LCII$) can be plotted as a function of immersion time, as shown in Figure 5.3. LCI can be calculated using equation 4.1 as described in Section 4.2. It could be seen in Figure 5.3 (b) that the $LCII$ of AA1100 fluctuated before it became larger at the later stages of exposure. It indicates that corrosion attack became more localised with the extension of corrosion exposure.

Figure 5.2 Changes of the (a) maximum and (b) total anodic current density of AA1100 with immersion time in 0.5 M NaCl solution

Figure 5.3 Changes of the (a) number of anodes and (b) localised corrosion intensity index of AA1100 with the immersion time in 0.5 M NaCl solution

In order to simulate a contaminated corrosion environment, which is common in practice, AA1100 WBE was studied by exposing to a neutral sodium chloride solution with 0.025% copper sulphate added as contaminates. WBE current and SRET maps are shown in Figure 5.4. It could be seen that galvanic currents increased dramatically with the presence of copper ions, compared with that in Figure 5.1. The maximum anodic current density in Figure 5.4 is much larger (0.351 mA/cm^2) than that in Figure 5.1 (0.028 mA/cm^2).

The SRET maps, as shown in Figures 5.4 (b) and (d), were also able to show some large anodic sites. In this corrosion system, anodic sites and cathodic sites were distinctly separated, which was resulted from macro-cell electrochemical activities, and the corrosion currents were large enough for SRET measurements. However, it appeared that SRET could not detect the anodic sites as sensitively as the WBE. The WBE map appeared to be able to show more details regarding anode distribution.

In this sense, WBE method seemed to be able to provide more information on the corrosion system being investigated. The conductivity of the sodium chloride solution with copper ions was high. In such a high conductivity solution, the sensitivity of SRET is usually poor. These facts may have led to a relative poor correlation between the WBE and SRET maps in Figure 5.4.

Figure 5.4 (a) Galvanic current distribution and (b) SRET maps obtained after 1 hr, and (c) galvanic current distribution and (d) SRET maps obtained 24 hrs immersion in 0.5 M NaCl + 0.025% CuSO_4 solution

5.1.2 AA1100 Corrosion with Copper Deposition at Specific Sites

In order to further understand the behaviour of aluminium corrosion with a second noble phase on its surface and to interpret the results in Figure 5.4, a WBE with pre-deposition of copper was employed. Metallic copper was deposited onto some specific wires of a WBE surface to artificially delineate cathodes on the WBE surface, as shown in Figure 5.5. WBE was prepared with copper deposition on either one wire – wire 57 (to simulate a small noble phase) or several wires – wire 34 to 37 and 44 to 47 (to simulate a large noble phase).

Figure 5.5 Deposition of copper on AA1100 WBE surface

The effects of pre-deposited copper were clearly detected by the WBE technique. As shown in Figure 5.6 (a) and (c), the major cathodic site clearly corresponded to the location of copper deposits on the WBE work surface, although no anodic and cathodic regions were detected by the SRET, as shown in Figure 5.6 (b). An explanation to this result is that the SRET was not sensitive enough to detect ionic currents in high conductivity 0.5M sodium chloride solution.

Figure 5.6 (a) WBE and (b) SRET maps obtained after 2 hrs, and (c) WBE map obtained after 4 hrs immersion in 0.5 M NaCl solution over AA1100 WBE surface with copper deposition on wire 57

For a WBE surface with pre-deposition of relatively large artificial cathode (copper on wire 34-37 and 44-47), corrosion had been driven by the large artificial cathode, as shown in Figure 5.7. Around this artificial cathode, anodes with relatively large current densities (from 0.062 to 0.036 mA/cm^2) were detected, as shown in Figure 5.7 (a), (c) and (d). It was noted that the measured maximum anodic current density of each WBE reading was often observed around the artificial cathode. Again, SRET was still not able to detect any electrochemical activity on WBE surface, as shown in Figure 5.7 (b). Compared with pure AA1100 corrosion (Figure 5.1), the

existence of the pre-deposited copper phase has caused a major increase in anodic currents: i_{max} increased from 0.027 mA/cm^2 in Figure 5.1 (c) to 0.049 mA/cm^2 in Figure 5.6 (a) and 0.042 mA/cm^2 in Figure 5.7 (c).

Figure 5.7 (a) WBE and (b) SRET maps obtained after 1 hr, and WBE maps obtained after (c) 4 hrs and (d) 8 hrs immersion in 0.5 M NaCl solution over AA1100 WBE surface with copper deposition on wire 34-37 and 44-47 as artificial cathode

It is interesting to note that corrosion attack on AA1100 in sodium chloride solutions containing cupric ions (Figure 5.4) is much more severe than that of pre-deposited AA1100 WBE in pure sodium chloride solution (Figure 5.6 and 5.7). Obviously, this is because the cupric ions contributed significantly to the cathodic reaction:

This cathodic reaction has led to rapid corrosion of AA1100, as shown in Figure 5.4.

5.1.3 AA1100 Corrosion under Anodic Polarisation

To study localised corrosion that occurs over AA1100 surface in chloride media further, anodic polarisation, which could accelerate the breakdown of the passive film or could repassivate AA1100 surface, was applied. WBE in conjunction with SRET measurements were applied to monitor the changes of corrosion behaviour under various anodic polarisation conditions, which included anodic polarisation below and above pitting potential.

Cyclic potentiodynamic polarisation was carried out to measure the pitting potential (E_{pit}). Cyclic potentiodynamic polarisation was carried out in aerated 0.5M sodium chloride solution at a sweep rate of 10 mV/min using a one-piece electrode of AA1100 with an area of about 1.21 cm², which was polished with 180, 320, 800, and 1000 grit silicon carbon paper and rinsed with deionised water, degreased with ethanol, and dried in air.

It could be seen that in 0.5 M sodium chloride solution, as shown in Figure 5.8, AA1100 electrode had an open circuit potential of approximately -920 mV vs. SCE and a pitting potential of approximately -760 mV, which agrees well with the pitting potential measurements made by others [Bond 1981].

Figure 5.8 Cyclic potentiodynamic polarisation of AA1100 in 0.5 M NaCl solution

WBE specimen made from AA1100 was immersed in 0.5 M sodium chloride solution for 1 hour, before external anodic polarisation was applied. The WBE map in Figure 5.9 (a) shows the random distribution of anodic sites over the specimen surface before anodic polarisation was applied. Again, SRET could not detect any electrochemical process, as shown in Figure 5.9 (b), under this free corrosion condition. After 1 hour immersion in 0.5 M sodium chloride solution, AA1100 was anodically polarised.

Figure 5.9 (a) WBE and (b) SRET maps at open circuit potential (-867 mV vs. SCE) (c) WBE and (d) SRET maps under anodically polarisation to -767 mV vs. SCE and (e) WBE and (f) SRET maps under anodically polarisation to -747 mV vs. SCE in 0.5 M NaCl solution

When the WBE surface was anodically polarised to -767 mV (100 mV above the open circuit potential but about 7 mV below the pitting potential), the WBE map indicated that anodic dissolution was accelerated with the maximum anodic dissolution current density increased from 0.048 to 0.28 mA/cm², as shown in Figure 5.9 (c). It was interesting to note that anodic dissolution sites remained almost unchanged after the application of anodic polarisation. The SRET was still unable to detect any ionic current in the electrolytic phase, Figure 5.9 (d).

When anodic polarisation of the WBE surface was further increased to -747 mV (13 mV above the pitting potential), as shown in Figure 5.9 (e), anodic dissolution current densities were further increased to a maximum value of 0.718 mA/cm². SRET measurements were able to detect anodic dissolution processes, as shown in Figure 5.9 (f), revealing similar anodic dissolution behaviour to that in the corresponding WBE map. Again the anodic dissolution sites remained almost unchanged.

It was surprising to note that the number of main anodic sites over the WBE surface decreased with the increase in polarisation voltage. For instance, the numbers of main anodes shown in Figures 5.9 (c) and 5.9 (e) are 9 and 5 respectively. This result was not in agreement with the conventional understanding on localised corrosion initiation, since it is generally believed that new localised anodic sites should initiate when the electrode was polarised to a potential above pitting potential. This result suggests a mechanism of localised corrosion formation – a process that minor anodes disappear, and thus anodic dissolution currents concentrate on a few remaining anodes. This result is reproducible and similar pitting initiation mechanism has been observed in other experiments of studying localised corrosion related electrochemical noise [Tan *et al.* 2004].

The SRET map in Figure 5.9 (f) also revealed another phenomenon that SRET was

able to detect ionic currents and their distribution when a WBE surface was polarised above its E_{pit} . This result suggests that the SRET could be used to detect E_{pit} , and at the same time, corrosion pattern.

When anodic polarisation was removed and thus aluminium WBE corrosion returned to free corrosion status, as shown in Figure 5.10, the WBE patterns became similar to that in Figure 5.9 (a) and the SRET map became ‘empty’ again. A difference between Figure 5.9 (a) and Figure 5.10 (a) was that some new major cathodes formed during the anodic polarisation processes. The mechanism behind this change is not clear and requires further investigation.

Figure 5.10 After the removal of anodic polarisation in 0.5 M NaCl solution

In summary, WBE was able to monitor corrosion process that was taking place over AA1100 surface, while SRET was not sensitive enough for detecting such corrosion processes. The measured WBE anodic current densities over the AA1100 surface in 0.5 M sodium chloride solutions were generally in the range of 10 to $0.1 \mu\text{A}/\text{cm}^2$. With the aid of anodic polarisation, SRET was able to detect the potential variations caused by ionic currents in the electrolyte when a WBE surface was polarised above its pitting potential. It suggests that the SRET can be used as an *in-situ* method to detect E_{pit} as well as the pitting profile.

5.2 Studies on the Corrosion of AA2024-T3

AA2024-T3 is a high strength aluminium alloy, which is prepared by intentionally adding elements, such as copper and magnesium into aluminium, to optimise mechanical properties. Generally, two types of intermetallic particles (phases) form during the alloying process, i.e. Al-Cu-Mg-containing phase (S-phase) particles, and Al-Cu-Fe-Mn-containing phase particles. Such heterogeneous microstructures have been found to make AA2024-T3 prone to localised attack [Buchheit *et al.* 1997; Blanc and Mankowski 1998; Aballe *et al.* 2001]. In order to achieve better understanding on this important aluminium alloy, AA2024-T3 corrosion in sodium chloride solutions has been investigated using the WBE in combination with SRET.

5.2.1 Corrosion of AA2024-T3 in 0.005 M Sodium Chloride Solution

A WBE fabricated from AA2024-T3 was exposed to 0.005 M sodium chloride solution using an experimental setup shown in Figure 3.6. Galvanic current distribution was measured via metallic phase using the WBE, and the potential variation through the electrolyte was measured using the SRET.

Corrosion pattern was found to be localised during the whole period of immersion, as shown in Figure 5.11. At the beginning of the exposure, as shown in Figure 5.11 (a) and (b), corrosion anodes appeared to be distributed in a random manner, corresponding to the distribution of the intermetallic particles, as shown in Figure 5.12. Energy Dispersive X-ray Spectroscopy (EDS) analysis revealed that most of these corroded intermetallic particles were S phase particles, as shown in Figure 5.12 (b) to (e). Distribution of the anodes detected by WBE and SRET measurements appeared to correspond to the distribution of the S phase particles. Both the WBE and SRET maps show that major anodes kept almost unchanged during the 48 hours exposure, although some minor anodes disappeared during the period. The most serious attack was observed at wire 61 of the WBE specimen, where the anodic current density was found to reach the maximum value of 0.113 mA/cm^2 after 12 hours immersion before decreasing to 0.095 mA/cm^2 .

Figure 5.11 Galvanic current distribution maps and SRET maps obtained in 0.005 M NaCl after 1 hr (a) WBE map (b) SRET map, 12 hrs (c) WBE map (d) SRET map, and 48 hrs (e) WBE map (f) SRET map

(a) AA2024-T3 surface after being immersed in 0.005 M NaCl solution for 1 hr

(b) Enlarged image of dealloyed S phase particles

(c) EDS analysis

(d) Enlarged image of dealloyed S phase particles

(e) EDS analysis on AA2024-T3 before immersion

Figure 5.12 (a) to (d) SEM observation and EDS analysis of AA2024-T3 after being immersed in 0.005 M NaCl solution for 1 hr (e) EDS spectrum obtained on AA2024-T3 before immersion in 0.005 M sodium chloride solution

Compared with the EDS result obtained on AA2024-T3 before immersion in 0.005 M sodium chloride solution, as shown in Figure 5.12 (e), it could be found that the peak of magnesium became much shorter after AA2024-T3 had been immersed in 0.005 M sodium chloride solution for 1 hr (as shown in Figure 5.12 (c)). The change of the ratios of the copper and magnesium peaks before and after immersion indicated that AA2024-T3 preferentially dealloyed magnesium at this stage. Other researcher also reported that S phase particles would dealloy in sodium chloride solution, leaving copper rich remnant [Buchheit *et al.* 1997; Schmutz and Frankel 1998; Dimitrov *et al.* 2000; Suter and Alkire 2001; Zhu and van Ooij 2003].

Figure 5.13 (a) shows changes of the number of anodes in WBE maps shown in Figure 5.11 with immersion time. It could be seen that the number of anodes decreased significantly with exposure time, indicating that corrosion became more concentrated. The localisation index also showed that the corrosion attack became more localised with immersion time, as shown in Figure 5.13 (b). Indeed, as shown in Figure 5.11, some of the minor anodes in Figure 5.11 (a) disappeared with the extension of exposure (Figure 5.11 (e)), although the position of major anodes kept unchanged. Changes of the maximum and total anodic current densities with the immersion time are shown in Figure 5.14. The total anodic current densities kept increasing within the first 12 hours immersion and then decreased. However, the maximum anodic current density remained at a high value after a significant increase in the first 12 hours. This result suggests that corrosion became more localised with exposure. The rapid increase in maximum and total anodic current densities during the first several hours of exposure could be associated with the initiation of the localised corrosion attack, which will be discussed in more details in section 5.3.

Figure 5.13 Changes of the (a) number of anodes and (b) localised corrosion intensity index with immersion time of AA2024-T3 in 0.005 M NaCl solution

Figure 5.14 Changes of the (a) maximum and (b) total anodic current density with immersion time of AA2024-T3 in 0.005 M NaCl solution

5.2.2 Corrosion of AA2024-T3 in 0.05 M and 0.5 M Sodium Chloride Solutions

The corrosion behaviour of AA2024-T3 in more concentrated sodium chloride solutions, i.e. 0.05 M and 0.5 M sodium chloride solutions, has also been studied by means of WBE and SRET measurements. As shown in Figures 5.15 and 5.16, severe localised attack on AA2024-T3 occurred in 0.05 M and 0.5 M sodium chloride solutions. In 0.05 M sodium chloride solution, the maximum anodic current density obtained immediately after immersion was 0.061 mA/cm^2 , and that obtained in 0.5 M sodium chloride solution was 0.112 mA/cm^2 , whilst that obtained in 0.005 M sodium chloride was only 0.018 mA/cm^2 (Figure 5.17 (a)). Comparisons of the maximum and total anodic current density changes in 0.005 M, 0.05 M, and 0.5 M sodium chloride solutions are shown in Figure 5.17. It could be seen clearly that the total anodic current densities of AA2024-T3 in 0.05 M and 0.5 M sodium chloride solution were similar to that in 0.005 M sodium chloride solution at the initial stage of immersion. After 48 hours corrosion exposure, they had similar values (0.4152 mA/cm^2 in 0.05 M sodium chloride, 0.4799 mA/cm^2 , and 0.43317 mA/cm^2 in 0.005 M sodium chloride solution). It indicates that the extent of total corrosion attack on AA2024-T3 alloy (dealloying of S phase particles) was relatively independent on the concentration of chloride ions present in the solutions, whilst the maximum corrosion attack at some specific area appeared to be dependent on the concentration of chloride ions. The more concentrated the chloride ions in the solution, the larger the maximum corrosion rate.

Figure 5.15 WBE maps obtained after (a) 1 hr, (b) 2 hrs, (c) 8 hrs, and (d) 48 hrs immersion in 0.05 M NaCl solution

Figure 5.16 WBE maps obtained after (a) 1hr, (b) 2 hrs, (c) 4 hrs, (d) 24 hrs, (e) 48 hrs and (f) SRET maps for 4 hrs immersion in 0.5 M NaCl solution

Changes of the number of anodes and localised corrosion intensity index with immersion time are shown in Figure 5.18. It shows that corrosion attack occurred in 0.5 M sodium chloride solution was much more localised. Figure 5.18 also shows that the localised corrosion intensity index increased rapidly at the initial stages of exposure in all of the three different concentrations of sodium chloride solutions.

Corrosion of AA2024-T3 in 0.5 M sodium chloride solution appeared to be the most localised. Localised corrosion intensity index of 0.05 M sodium chloride was a bit smaller than that of 0.005 M sodium chloride solution was due to the much larger number of anodes. However, the reason for corrosion became relatively more general (more anodes) in 0.05 M sodium chloride solution is unclear and needs further investigation.

Although the measured maximum corrosion current density in 0.5 M sodium chloride solution was large, 0.282 mA/cm^2 (Figure 5.16 (c)), which was much higher than that in 0.005 M sodium chloride solution (0.113 mA/cm^2 , Figure 5.11 (c)), the SRET was unable to detect the corrosion process, as shown in Figure 5.16 (f). Comparison of Figure 5.16 (f) and Figure 5.11 (d) confirms that high conductivity of 0.5 M sodium chloride solution has significantly affected the sensitivity of SRET measurement.

Figure 5.17 Changes of the (a) maximum and (b) total anodic current density with immersion time of AA2024-T3 in various sodium chloride solutions

(a)

(b)

Figure 5.18 Comparison of the (a) number of anodes and (b) localised corrosion intensity index of AA2024-T3 in 0.005 M, 0.05 M, and 0.5 M NaCl solutions

5.3 Analysing the Behaviour and Mechanism of AA1100 and AA2024-T3 Corrosion

The main difference of aluminium (AA1100) and its alloys (AA2024-T3) is their composition and microstructure. From SEM observation, as shown in Figure 5.19(a) and (b), it could be seen that AA2024-T3 contains a lot of intermetallic particles. These particles are aluminium-depleted, as shown in the elements distribution of AA2024-T3 maps in Figure 5.19 (c), and copper-rich. Of all the particles, those containing Cu, Fe and Mn elements were the Al-Cu-Fe-Mn particles, while those containing Cu and Mg elements were the S phase particles. It could be seen that there were more Al-Cu-Fe-Mn particles than Al-Cu-Mg particles in the alloy. Moreover, Al-Cu-Fe-Mn particles were usually larger than Al-Cu-Mg (S phase) particles. The large S phase particle has size of only about several micrometers, while some of Al-Cu-Fe-Mn particles are as large as more than 10 micrometers. It has also been reported that the Cu-containing phase particles could start to act as local anodes or cathodes on the surface as soon as the alloy is exposed to aqueous environments [Buchheit *et al.* 1997; Suter and Alkire 2001; Waldroop and Kendig 1998]. Such particles could not be observed on pure aluminium AA1100, as shown in Figure 5.20, although it has been reported that second phase particles containing Fe or Fe and Si (Al_6Fe , Al_3Fe , and $\text{Al}_{12}\text{Fe}_3\text{Si}_2$), which are cathodic to the aluminium matrix, could be present [Davis 1999]. It should be due to the much less content of the alloying elements in AA1100.

Figure 5.19 (a) and (b) general view of the intermetallic particles, and (b) mapping of elements distribution of AA2024-T3.

Figure 5.20 SEM observation and EDS analysis of AA1100 before exposed to sodium chloride solution

Polarisation curve obtained from AA2024-T3 electrode after 1 hour immersion in the aerated 0.005 M sodium chloride solutions is shown in Figure 5.21. Compared with the polarisation curves of AA1100 in Figure 5.8, the corrosion current of AA2024-T3 electrode shown in Figure 5.21 is much larger. This may suggest that the presence of active anodic and cathodic intermetallic particles in AA2024-T3 leads to an increase in corrosion activities.

Figure 5.21 Potentiodynamic polarisation curve of AA 2024-T3 in the aerated 0.005M NaCl solution

Compared with AA1100 (Figure 5.1), corrosion of AA2024-T3 in 0.5 M (as shown in Figure 5.22) and 0.005 M (as shown in Figure 5.23) sodium chloride solutions was very severe. It could be seen clearly that the existence of the intermetallic particles has influenced the corrosion behaviour of aluminium alloy significantly. Figures 5.22 and 5.23 show that AA2024-T3 corrosion process includes a formation period, which is manifested by the rapid increases on both the maximum and total anodic current density curves. The term of “formation period” in this thesis is defined as the period that after the pit nucleation and meta-stable pit while before major growth of pits, since the techniques used in this thesis is not able to detect the pit nucleation and meta-stable pits. The rapid increase in anodic currents during this period should be due to the dissolution of the intermetallic particles or the dissolution of aluminium matrix around the intermetallic particles, as shown in Figure 5.12.

Figure 5.22 Comparison of the (a) maximum and (b) total anodic current densities obtained from AA1100 and AA2024-T3 WBEs exposed to 0.5 M NaCl solution

Figure 5.23 Comparison of the (a) maximum and (b) total anodic current densities obtained from AA1100 and AA2024-T3 WBEs exposed to 0.005 M NaCl solution

With the extension of corrosion exposure, dissolution of intermetallic particles or the

surrounding aluminium became serious, as shown in Figures 5.24 to 5.28.

(a) General view of AA2024-T3 in 0.005 M for 2 hrs

(b) S phase particles

(c) No severe corrosion can be observed at or around the Al-Cu-Fe-Mn particles

(d) pit formed on AA1100 in 0.5 M NaCl

(e) corrosion products at the pit of AA1100

Figure 5.24 SEM observation of AA2024-T3 ((a) to (c)) after being immersed in 0.005 M NaCl for 2 hrs, and AA1100 ((d) and (e)) in 0.5 M NaCl for 48hrs

It can be seen that morphologies of the corroded AA2024-T3 and AA1100 are different, as shown in Figure 5.24 (a) and (d). Corrosion usually attacks AA2024-T3 at or around the intermetallic particles (Figure 5.24 (a) to (c)). Corrosion attacks AA1100 surface randomly (Figure 5.24 (d) and (e)), and appeared to be dependent on the behaviour of breakdown of the passive film [Frankel 1998; Davis 1999; Szklarska-Smialowska 1999].

After exposure of AA2024-T3 to sodium chloride solution was extended to 4 hours, corrosion attacks on AA2024-T3 surface expanded to include areas around the Al-Cu-Fe-Mn particles, as shown in Figure 5.25. It indicates that corrosion became more serious, corresponding well with the rapid increase in both maximum and total anodic current densities (Figure 5.23).

Figure 5.25 SEM observation of AA2024-T3 after being immersed in 0.005 M NaCl solution for 4 hrs

When AA2024-T3 exposure was extended to 12 hours, as shown in Figure 5.26, much more severe localised corrosion attacks could be observed at or around almost

all visible intermetallic particles, including both the S phase particles and Al-Cu-Fe-Mn particles. Moreover, some microcracks, which seem to be spreading into the surrounding aluminium matrix, could also be observed around the corroded particles.

Figure 5.26 SEM observation of AA2024-T3 after being immersed in 0.005 M NaCl solution for 12 hrs

When AA2024-T3 was exposed to sodium chloride solution for 24 hours (Figure 5.27) and for 48 hours (Figure 5.28), there was still no visible corrosion on the main aluminium matrix.

Figure 5.27 SEM observation of AA2024-T3 after being immersed in 0.005 M NaCl solution for 24 hrs

Figure 5.28 SEM observation of AA2024-T3 after being immersed in 0.005 M NaCl solution for 48 hrs

SEM observation clearly indicates that AA2024-T3 corrosion in sodium chloride solution took place at or around the intermetallic particles, forming microcrevices. Thus, it can be concluded that the corrosion process of AA2024-T3 in sodium chloride solution was mainly governed by the presence of intermetallic particles. However, for relatively pure aluminium such as AA1100, which has nearly no intermetallic particles (as shown in Figure 5.20), the corrosion process was predominated by random breakdown of the passive film [Szklańska-Smiałowska 1999].

Based on WBE and SRET maps and SEM/EDS analysis presented above, the corrosion mechanism of AA2024-T3 can be described as followings. At the initial stages of corrosion exposure, AA2024-T3 corrosion usually occurs at the S phase particles leading to the formation of microcrevices between the particles and the surrounding aluminium matrix. This is in agreement with the results reported by other researchers [Buchheit *et al.* 1997; Leblanc and Frankel 2002; Zhu and van Ooij

2003] that localised attack always initiates by S phase dealloying when AA2024-T3 is expose to neutral sodium chloride solutions. Once the microcrevices are formed, a synergetic process of dealloying, crevice corrosion and cathodic corrosion may take place. It is reasonable to expect that the corrosion current increases gradually with the S phase dealloying process. Corrosion caused by the establishment of galvanic corrosion system between the small copper rich remnant (formed by the preferentially dealloying Al and Mg at S phase particle) and the adjacent aluminium matrix is negligible due to the small cathode-to-anode area ratio. The mechanism by which corrosion takes place at and around the S phase particles is schematically illustrated in Figure 5.29.

Figure 5.29 Schematic illustration of corrosion mechanism around S phase particle of AA2024-T3 in sodium chloride solution

Step I. On the surface of S phase particles, corrosion initially takes place by dealloying Al and Mg leading to increase in pH around the S phase particles [Vukmirovic *et al.* 2002; Zhu and van Ooij 2003] and on the surface of Al-Cu-Fe-Mn particles (most cathodic intermetallic particles in AA2024-T3) because of the occurrence of cathodic reaction.

- Anodic reactions: Al and Mg dealloying

- Cathodic reaction: oxygen reduction and hydrogen evolution occur at the Al matrix around dealloying S phase particles and on the surface of Al-Cu-Fe-Mn particles

- Copper rich remnant is generated by the dealloying of S phase particles.

Step II. Cathodic corrosion, leading to the formation of microcrevices around S phase particles and Al-Cu-Fe-Mn particles, occurs due to high pH.

A high pH (when pH exceeds ~9) causes aluminium oxide film to dissolve chemically due to the alkalinity generated by the hydrogen evolution and oxygen reduction reactions [van de Ven and Koelmans 1976]. When the aluminium oxide film dissolves in the alkaline solution, new oxide film will form on the bare Al underneath: electrochemical process involving electron transfer, as expressed by the following reaction

This leads to continuous oxidation and corrosion of aluminium. This phenomenon is called cathodic corrosion [van de Ven and Koelmans 1976; Despic *et al.* 1990; Takahashi *et al.* 1994; Zhu and van Ooij 2003].

Step III. At the microcrevice, in oxygenated neutral sodium chloride solution, water reduction will occur on both the freely exposed surface and the surface within the crevice, once the corrosion has taken place [Shreir *et al.* b1994]. The freely exposed surface (outside the crevice) is accessible to dissolved oxygen by convection and diffusion. However, access of oxygen within the crevice is controlled by diffusion. Under this condition, oxygen concentrations outside and inside the crevice are quite different. Compared to that outside the crevice, oxygen concentration within the crevice is negligible, and a differential aerated corrosion cell is established. Crevice corrosion then takes place in the crevice. Hydrolysis of aluminium chloride occurs in the crevice leading to a reduction in pH of solution. Thus, a self-catalyst localised corrosion system is established.

Cathodic corrosion taking place on the aluminium matrix, which is in vicinity of the dealloyed S phase particle and near the crevice mouth, will contribute to the whole corrosion processes occurring around the S phase. It is noted that all the corrosion processes mentioned above are occurring at or around the S phase particles. This may be the reason for that the locations of the major anodes on the WBE and SRET maps (such as Figure 5.11) kept almost unchanged during the whole period of exposure. SEM observation also revealed that localised corrosion occurred at the S

phase particles, while no visible corrosion could be observed on the aluminium matrix that was far away from such particles. The WBE results, such as those in Figure 5.23, show that corrosion of AA2024-T3 in sodium chloride solution usually consists of two periods. At the formation period (usually the first 12 hours), the maximum and total anodic current densities kept increasing to very high values. At the later stages of exposure (propagation stage), the maximum and total anodic current densities decreased gradually, but still remain at high value. The S phase dealloying and microcrevice formation process corresponds well with the corrosion initiation stage shown in Figure 5.23.

It has been discussed above that corrosion attack of the S phase particle at the formation stage can take the form of dealloying of Al and Mg elements. With the extension of immersion, crevice corrosion starts to occur in the microcrevice and at the same time cathodic corrosion continues to be active outside the crevice, and thus the anodic current remains high.

It should be noted that with the extension of exposure, the S phase could create Cu-rich remnant due to the dealloying. It has been reported that such Cu-rich remnant could turn to efficient cathode and cause the dissolution of aluminium matrix surrounding it due to its noble potential with respect to the Al matrix [Buchheit *et al.* 1997]. In this mechanism, localised corrosion was considered to be resulted from the establishment of galvanic system between the aluminium matrix and the copper rich remnant. However, the S phase particles are generally very small – not more than several micrometers in size. If considering the cathode-to-anode area ratio, the corrosion rate of aluminium matrix caused by such small cathodic copper rich remnant should be insignificant.

Cathodic intermetallic particles – Al-Cu-Fe-Mn containing particles, appeared not to cause corrosion at the very beginning of immersion (Figure 5.24). Microcrevices

could only be observed around this type of particles after 4 hours immersion. It has been reported that the Al-Cu-Fe-Mn particles are the most cathodic particles in AA2024-T3, the aluminium matrix adjacent these particles are considered to be corroded due to the formation of galvanic corrosion cell between the particles and the aluminium matrix. However, from Figure 5.19, it could be seen that most of the Al-Cu-Fe-Mn particles were very small, only a few particles have sizes more than 10 micrometers. The anode-to-cathode area ratio was also very small, thus, the anodic current density resulted from galvanic corrosion should be very small. Similar to the case of the Cu-rich remnant, which is generated by the dealloying of the S phase particles, cathodic reaction can be concentrated on the Al-Cu-Fe-Mn particles, and pH is increased locally. Increase in pH and diffusion of OH⁻ ions to surrounding areas could cause cathodic corrosion on surrounding regions, leading to crevice corrosion.

Based on the above discussion, the corrosion attack occurring at and/or around the S phase and Al-Cu-Fe-Mn particles may be the synergetic process of cathodic corrosion, crevice corrosion, and dealloying. However, corrosion attack at S phase particles usually initiates in a form of dealloying followed by cathodic corrosion and crevice corrosion, while that around the Al-Cu-Fe-Mn particles usually initiates in a form of cathodic corrosion followed by crevice corrosion. The mechanisms can be summarised as:

1. Localised corrosion initiates at the S phase particles by dealloying; pH is increased in vicinity of the dealloying S phase particles and Al-Cu-Fe-Mn particles.
2. Cathodic corrosion occurs due to high pH (when pH is increased up to more than 9).
3. Microcrevices are formed around the S phase particles and Al-Cu-Fe-Mn particles.

4. Crevice corrosion occurs around the S phase particles and Al-Cu-Fe-Mn particles.
5. Dealloying of S phase particle stops; cathodic corrosion and crevice corrosion survive.

Steps 1 – 4 correspond to the formation stage showed on the maximum and total anodic current curves, step 5 corresponds to the propagation stage (Figure 5.23).

This can be clearly showed by the following flow chart.

AA2024-T3 is exposed to sodium chloride solution

CHAPTER 6

Results and Discussion II: Studies on the Inhibition of Aluminium Corrosion

6.1 The Performance and Mechanism of Dichromate Inhibition

Potassium dichromate is considered to be an effective inhibitor for inhibiting corrosion of aluminium and its alloys. However, the mechanism by which it inhibits aluminium corrosion is still not fully understood. In this work, the WBE in conjunction with SRET method together with traditional techniques such as polarisation techniques and scanning electron microscope, have been applied to investigate the performance and mechanism of dichromate inhibition.

6.1.1 The Effects of Dichromates on AA1100 Corrosion

WBE made from aluminium AA1100 has been exposed to neutral sodium chloride solutions containing 1000 ppm and 100 ppm potassium dichromate respectively. Experimental setup is shown in Figure 3.6. Figure 6.1 shows galvanic current distribution maps obtained from AA1100 WBE exposed to 0.5 M sodium chloride solution containing 1000 ppm potassium dichromate. It could be seen that in such a solution, corrosion sites distributed in a random manner during the whole exposure period. There were over 80 wires that were found to be anodes. Compared to that of AA1100 in pure sodium chloride solution (Figure 5.1), corrosion in the dichromate containing solution was much slower and more general. The largest anodic current density was only $7.352 \times 10^{-3} \text{ mA/cm}^2$, as shown in Figure 6.1 (a). Again, SRET

was not able to detect the corrosion process and an ‘empty’ map was obtained (not shown here).

Figure 6.1 AA1100 WBE maps obtained after (a) 1 hr, (b) 8 hrs, (c) 24 hrs, and (d) 48 hrs immersion in 0.5 M NaCl+1000 ppm $K_2Cr_2O_7$ solution

Figure 6.2 shows the WBE maps obtained from AA1100 when it was exposed to sodium chloride solution containing 100 ppm potassium dichromate. It could be seen that corrosion process taking place on AA1100 in such a solution was similar to that in 1000 ppm potassium dichromate containing solution.

Figure 6.2 AA1100 WBE maps obtained after (a) 1 hr, (b) 12 hrs, (c) 24 hrs, and (d) 48 hrs immersion in 0.5 M NaCl+100 ppm $\text{K}_2\text{Cr}_2\text{O}_7$ solution

In Figure 6.3, it could be found that at the beginning of exposure, the measured maximum anodic current densities (in a range of $\mu\text{A}/\text{cm}^2$) are similar to those in pure sodium chloride solution (Figure 5.1 (a) and (b)). The maximum anodic current densities were kept small in the dichromate containing solution during the whole exposure period. Without inhibitor, as shown in Figure 5.1 (c) to (e), anodic current densities showed major increase, indicating acceleration of corrosion. This result suggests that 1000 ppm potassium dichromate was efficient in inhibiting AA1100 corrosion.

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From Figure 6.3 (b), it could be found that the total anodic current densities in potassium dichromate containing solution had large initial values, while that in pure sodium chloride showed a gradual increasing trend. The large initial values of the total anodic current density are believed to be due to anodic process that was taking place on AA1100 surface, exposed to the potassium dichromate solutions, leading to passivation. The large initial anodic current density shown in the maximum current density curve of Figure 6.3 (a) should also be resulted from the passivation process.

Figure 6.4 shows changes of the number of anodes and localised corrosion intensity index with immersion time. Both of the number of anodes and localised corrosion intensity index indicate that without potassium dichromate, corrosion attack on AA1100 in 0.5 M sodium chloride solution was much more localised. This experiment result indicates that with the presence of potassium dichromate, most locations on the WBE surface were anodes and thus corrosion was less localised.

Figure 6.3 Comparison of changes of the (a) maximum and (b) total anodic current density with immersion time of AA1100 in 0.5 M NaCl solution with and without dichromates

Figure 6.4 Changes of the (a) number of anodes and (b) localised corrosion intensity index with immersion time of AA1100 in 0.5 M NaCl solution with and without inhibitors

The total anodic current density obtained from the WBE is the sum of all the anodic galvanic corrosion current density (i_{gk}). In Chapter 2, it has been discussed that when the difference between the open-circuit potential of a wire and the potential of the whole system is larger than 100 mV, $I_{gk} = I_{ka}$ (see equation 2.5). Since each wire of WBE has a same area, so it can be also expressed as: $i_{gk} = i_{ka}$. In this case (under large polarisation), the galvanic current density can be taken as an estimation of localised corrosion current density.

The inhibition efficiency (IE) of inhibitors can be estimated by,

$$IE = \frac{CR_0 - CR_{inhi}}{CR_0} \times 100 \quad (6.1)$$

where CR is corrosion rate. CR_0 is the corrosion rate in the sodium chloride

solution without any inhibitor, while CR_{inhi} is the corrosion rate with the presence of inhibitor. The corrosion rate can be calculated using Faraday's Law,

$$CR = k_1 \frac{i_{corr}}{\rho} EW \quad (6.2)$$

where i_{corr} is the corrosion current density, ρ is the density of the material, EW is equivalent weight, and k_1 is $3.27 \times 10^{-3} \text{ mm}\cdot\text{g}/\mu\text{A}\cdot\text{cm}\cdot\text{yr}$.

$$IE = \frac{i_{corr} - i_{inhi-corr}}{i_{corr}} \times 100 \quad (6.3)$$

i_{corr} and $i_{inhi-corr}$ are corrosion current densities without and with inhibitors respectively.

i_0 and i_{inhi} refer to the sums of anodic galvanic corrosion current density obtained without and with the presence of inhibitors respectively. Based on the assumption that galvanic corrosion density has a similar value to localised corrosion current density, it has

$$\text{Without inhibitor:} \quad i_0 = i_{tot} = \sum_{k=1}^n i_{gk} \approx i_{corr}$$

$$\text{With inhibitor:} \quad i_{inhi} = i_{tot-inhi} = \sum_{k=1}^n i_{gk-inhi} \approx i_{corr-inhi}$$

Thus, the inhibition efficiency of inhibitors can be estimated using

$$IE = \frac{i_0 - i_{inhi}}{i_0} \times 100 \quad (6.4)$$

The inhibition efficiency of different inhibitors can be estimated using equation 6.4, if the total current densities are known. As shown in Figure 6.3, i_0 (without any inhibitor) was approximately 0.0491 mA/cm², while $i_{Cr-1000}$ (namely i_{inhi} for AA1100 in 0.5 M sodium chloride with 1000 ppm potassium dichromate) and i_{Cr-100} (with 100 ppm potassium dichromate) were around 0.0219 mA/cm² and 0.038 mA/cm² respectively. **IE** can be calculated by substituting i_0 and i_{inhi} into equation 6.4:

$$IE_{Cr-1000} = [(0.0491 - 0.0219) / 0.0491] \times 100 \approx 55.4$$

$$IE_{Cr-100} = [(0.0491 - 0.038) / 0.0491] \times 100 \approx 22.6$$

This indicates that either the concentration of 1000 ppm or 100 ppm of potassium dichromate could inhibit AA1100 corrosion in 0.5 M sodium chloride solution.

In another experiment, AA1100 was immersed in 0.5 M sodium chloride solution for 24 hours before 100 ppm potassium dichromate was added to the solution. After being exposed to sodium chloride solution, stable major anodes were found to form on the WBE surface, as shown in Figure 6.5 (a). The maximum anodic current densities of the existing anodes were found to decrease slightly after the addition of inhibitor, as shown in Figure 6.5 (c), from 0.034 mA/cm² to 0.03 mA/cm², and then decrease further to 0.02 mA/cm² gradually, Figure 6.5 (d). In comparison with the case that potassium dichromate was present at the beginning of exposure; the inhibition efficiency of potassium dichromate was poor when it was introduced to the electrolyte at the later stages of exposure.

Figure 6.5 WBE maps obtained (a) after 24 hrs immersion in 0.5 M NaCl solution, and (b) 10 mins, (c) 2 hrs and (d) 24 hrs after the addition of 100 ppm $K_2Cr_2O_7$ into 0.5 M NaCl solution (WBE maps in a unit of mA/cm^2)

It was also noted that when 100 ppm potassium dichromate was added into the electrolyte, the measured maximum anodic current density was slightly decreased, as shown in Figure 6.5 and Figure 6.6 (a). However, it can be seen in Figure 6.6 (b) that the total anodic current density increased with the addition of potassium dichromate at later stage of the exposure. The sharp increase in anodic current densities is an interesting phenomenon that has been observed repeatedly and it might be due to the partial passivation of the metal surface by dichromates. Partial

passivation can result in more serious corrosion at the active sites that are not passivated by the potassium dichromate [Rozenfeld 1981a].

When dichromate ions are introduced into the solution, they can passivate the metal surface by

This process involves the dissolution of aluminium and an anodic current. Thus, large anodic dissolution current density is expected at the beginning of the addition of such inhibitors. When a passive film is formed, the anodic current density would decrease. This result also indicates that potassium dichromate behaved as an anodic inhibitor, because cathodic inhibitor would never intensify the corrosion process.

Figure 6.6 Changes of the (a) maximum and (b) total anodic current density as a function of immersion time in 0.5 M NaCl solution with the addition of 100 ppm $\text{K}_2\text{Cr}_2\text{O}_7$ at the later stages of the immersion

6.1.2 The Effects of Dichromates on AA2024-T3 Corrosion

Figure 6.7 shows the WBE and SRET maps obtained from an AA2024-T3 WBE exposed to a solution containing 1000 ppm potassium dichromate in 0.005 M sodium chloride solution. Corrosion rates decreased significantly in comparison with that in Figure 5.11. The measured maximum anodic current density during the whole period of the experiment was only 0.011 mA/cm^2 . It was about one order of magnitude smaller than that obtained in the sodium chloride solution without any inhibitors (0.113 mA/cm^2 , Figure 5.11 (c)). In the electrolyte containing dichromates, WBE maps show some stable anodes from the beginning to the end of experiment; meanwhile a lot of anodes with very small values of anodic current density can also be observed, as shown in Figure 6.7 (a) to (e). It could be seen that the anodic sites are randomly distributed over the WBE surface.

Figure 6.8 shows the changes of maximum and total anodic current density with immersion time. It could be seen that during the whole period of exposure, both the maximum and total anodic current densities were much smaller than those in pure sodium chloride. Compared with the pure sodium chloride solution, there were more anodes in the dichromate containing solution; however the total anodic current density was much smaller because of very small anodic current density of each anodic site. It illuminates that 1000 ppm potassium dichromate was effective in inhibiting aluminium dissolution in 0.005 M sodium chloride solution. From Figure 6.8, it is noted that there is an initial peak on the total anodic current density curve. This initial peak of anodic current density could be due to the passivation process, which could introduce a large anodic current density.

Figure 6.7 WBE maps obtained after (a) 10 mins, (b) 4 hrs (c) 12 hrs, (d) 24 hrs, and (e) WBE and (f) SRET maps after 48 hrs immersion in 0.005 M NaCl + 1000 ppm $\text{K}_2\text{Cr}_2\text{O}_7$ solution (WBE maps in a unit of mA/cm^2)

Figure 6.8 Comparison of the (a) maximum and (b) total anodic current density with immersion time of AA2024-T3 in 0.005 M NaCl + 1000 ppm $K_2Cr_2O_7$ solution

In this experiment, SRET map was again not able to show any obvious anodic and cathodic sites, as shown in Figure 6.7 (f), probably due to the small current density.

Comparison of the localised corrosion intensity index of AA2024-T3 in 0.005 M sodium chloride solution with and without the presence of 1000 ppm potassium dichromate was shown in Figure 6.9 (b). It could be seen that with the presence of potassium dichromate, corrosion of AA2024-T3 in sodium chloride solution became more general.

Figure 6.9 Changes of the (a) number of anodes and (b) localised corrosion intensity index with immersion time

As shown in Figure 6.8 (b), the i_0 of AA2024-T3 exposed to 0.005 M sodium chloride solution for 48 hours is approximately 0.4332 mA/cm^2 . With the addition of 1000 ppm potassium dichromate, as shown in Figure 6.8 (b), the i_{inhi} is approximately 0.0075 mA/cm^2 . Hence, **IE** can be calculated by substituting i_0 and i_{inhi} into equation 6.4:

$$IE = [(0.4332 - 0.0075) / 0.4332] \times 100 \approx 98.26$$

This indicates that 1000 ppm potassium dichromate inhibits AA2024-T3 corrosion in 0.005 M sodium chloride solution with high efficiency. SEM observation and EDS analysis of AA2024-T3 sample have been carried out after it was immersed in 0.005 M sodium chloride solution containing 1000 ppm potassium dichromate for 48 hours. No obvious localised corrosion and microcracks could be found over the entire metal surface, as shown in Figure 6.10, confirming the efficiency of 1000 ppm potassium dichromate.

Figure 6.10 SEM image of AA2024-T3 surface after exposed to the solution of 0.005 M NaCl + 1000 ppm K₂Cr₂O₇ for 48 hrs

Potentiodynamic polarisation of AA2024-T3 has been carried out in 0.005 M sodium chloride solution containing 1000 ppm potassium dichromate, as shown in Figure 6.11. It can be seen that the polarisation curve of AA2024-T3 in sodium chloride solution containing dichromates is quite different from that obtained in sodium chloride solution without inhibitor. With the presence of dichromate ions, the polarisation curve becomes smooth. Sharp increase in current density is only observed at approximately -310 mV (SCE), indicating the breakdown of the chromium-rich passive film. It has been reported [Kolics *et al.* 2001b; Frankel and McCreery 2001; Leblanc and Frankel 2002; Chidambaram *et al.* 2003] that when AA2024-T3 was exposed to dichromate containing solution, a chromium-rich film could form on the entire specimen surface, especially on the active S phase particles, inhibiting both the anodic and cathodic reactions. Since the chromium-rich film covered the entire surface and protected the aluminium alloy underneath, the corrosion behaviour of AA2024-T3 in sodium chloride solution was then mainly determined by this protective film. The effects of S phase and Al-Cu-Fe-Mn particles were minimised and thus a smooth polarisation curve was obtained.

Figure 6.11 Potentiodynamic polarisation curve of 2024-T3 obtained in 0.005 M NaCl + 1000 ppm $K_2Cr_2O_7$ solution.

100 ppm potassium dichromate was also used to inhibit AA2024-T3 corrosion in 0.005 M sodium chloride solution. With the addition of 100 ppm potassium dichromate in 0.005 M sodium chloride solution, corrosion rate of AA2024-T3 decreased, as shown in Figure 6.12. The measured maximum anodic current density after 48 hours of exposure was only 0.011 mA/cm^2 , and was about one order of magnitude smaller than that obtained in the non-inhibiting sodium chloride solution (0.113 mA/cm^2 , Figure 5.11 (c)).

Figure 6.12 WBE maps obtained after (a) 10 mins, (b) 1hr, (c) 24 hrs and (d) 48 hrs immersion in 0.005 M NaCl + 100 ppm K₂Cr₂O₇ solution

Changes of the maximum and total anodic current densities with immersion time are shown in Figure 6.13. Initial large current peaks could be observed on both the maximum and total anodic current density curves. It may be due to the passivation process occurring over the specimen surface at the beginning of exposure.

The *IE* value of 100 ppm potassium dichromate in such system can also be calculated using equation 6.4. i_{inhi} is approximately 0.0175 mA/cm², then

$$IE = [(0.4332 - 0.0175) / 0.4332] \times 100 \approx 95.96$$

It could be seen that 100 ppm potassium dichromate has a similar effectiveness to 1000 ppm potassium dichromate at inhibiting AA2024-T3 corrosion in 0.005 M sodium chloride solution. However, the pattern of AA2024-T3 corrosion in 100 ppm and 1000 ppm potassium dichromate containing solutions are very different.

Figure 6.14 shows changes of the number of anodes and localised corrosion intensity index with the immersion time. It could be found that in 100 ppm potassium dichromate containing solution, corrosion became much more localised in comparison with that in sodium chloride solution or sodium chloride solution with 1000 ppm potassium dichromate. It indicates that corrosion of AA2024-T3 in 0.005 M sodium chloride solution with 100 ppm potassium dichromate was more localised, possibly due to the partial passivation of AA2024-T3 surface by a relatively low concentration of potassium dichromate. Potassium dichromate may not be able to fully passivate the entire AA2024-T3 surface when it is used at the concentration of 100 ppm in 0.005 M sodium chloride solution.

Figure 6.13 Comparison of the (a) maximum and (b) total anodic current density in 0.005 M NaCl solution without and with 100 ppm and 1000 ppm K₂Cr₂O₇

Figure 6.14 Changes of the (a) number of anodes and (b) localised corrosion intensity index with immersion time

In another experiment, inhibition of potassium dichromate on the corrosion behaviour of AA2024-T3 in 0.005 M sodium chloride solution was studied by adding 1000 ppm potassium dichromate to the sodium chloride solution at the later stages of experiment. After AA2024-T3 had been immersed in 0.005 M sodium chloride solution for 24 hours, 1000 ppm potassium dichromate was added. Figure 6.15 shows the changes of AA2024-T3 corrosion behaviour before and after the addition of potassium dichromate. As shown in Figure 6.15, the maximum anodic current density increased dramatically at the very beginning of the inhibitor addition. Some of the anodes, which have existed before the addition of dichromates, disappeared with further immersion. After 24 hours exposure to the solution containing dichromates, the main anodes still exist but with much smaller current densities. It was also found that if potassium dichromate was added at later stages of exposure, it was not as efficient as it was added at the beginning of exposure.

Figure 6.15 (a) WBE maps of AA2024-T3 obtained after 24 hrs immersion in 0.005 M NaCl solution, (b) to (f) obtained in the solution of 0.005M NaCl with the addition of 1000 ppm K₂Cr₂O₇ later, WBE maps obtained after (b) 10 mins, (c) 1hr, (d) 4 hrs, (e) 8hrs and (f) 24 hrs (WBE maps in a unit of mA/cm²)

Figure 6.16 shows changes of the maximum and total anodic current densities with the immersion time. It could be seen that both the maximum and total anodic current density increased significantly, immediately after the addition of potassium dichromate into the sodium chloride solution. For instance, the maximum anodic current density measured before the addition was only 0.079 mA/cm^2 , as shown in Figure 6.15 (a), jumped to 0.232 mA/cm^2 immediately after the inhibitor addition. It decreased to 0.017 mA/cm^2 after 24 hours (Figure 6.15 (f)). This result suggests that the dissolution of aluminium was accelerated by the addition of inhibitor. The sharp increase in anodic current densities (both the maximum and total current densities) caused by the addition of dichromate should be due to the anodic reaction of the metal surface by dichromates, leading to passivation of AA2024-T3 surface. Similar to the case of AA1100 (Figure 6.6), potassium dichromate behaved as an anodic inhibitor for AA2024-T3 in sodium chloride solutions.

SEM photograph shown in Figure 5.27 indicates that many microcrevices formed after AA2024-T3 immersion in 0.005 M sodium chloride solution for 24 hours. The difficulty for potassium dichromate to reach the aluminium matrix within these microcrevices could have resulted in partial passivation of AA2024-T3 surface when potassium dichromate was first introduced into the electrolyte. This process could cause rapid dissolution of aluminium within the microcrevices and contribute to the sharp increase of anodic current immediately after the addition of potassium dichromate.

In addition to the microcrevices created during the exposure of WBE to sodium chloride solution, corrosion products could behave as a barrier for dichromate ions to reach the aluminium surface, and thus the free access of the inhibitor to all parts of the specimen surface at the initial stage of addition cannot be ensured. It could take some time for the dichromates to penetrate the corrosion products, to reach the

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aluminium substrate, and then to passivate the aluminium. In this case, anodic dissolution was intensified before potassium dichromate was achieved. This is schematically illustrated in Figure 6.17.

Figure 6.16 Changes of the (a) maximum and (b) total anodic current density with immersion time of AA2024-T3 with 1000 ppm $K_2Cr_2O_7$ added at the later stages of exposure to 0.005 M NaCl solution

Figure 6.17 Schematic showing the situation around dealloying S phase particle when potassium dichromate is added at the later stages of exposure

The **IE** value can be estimated using equation 6.4. i_0 has a value of approximately 0.545 mA/cm² (as shown in Figure 6.16 (b)), and i_{inhi} , the total anodic current density that obtained after the addition of 1000 ppm potassium dichromate for 24 hours, has a value of approximately 0.0099 mA/cm². Thus, **IE** is thus calculated as:

$$IE = [(0.545 - 0.0099) / 0.545] \times 100 \approx 81.89$$

The lower **IE** value indicates that 1000 ppm potassium dichromate was not as effective as the case when dichromates are present at the beginning of experiment.

In order to confirm the correctness of the above analysis, another experiment was carried out by adding 1000 ppm potassium dichromate after AA2024-T3 had been exposed to 0.005 M sodium chloride for only 1 hour. Figure 6.18 shows the WBE maps obtained before and after the addition of 1000 potassium dichromates. It can be seen that the maximum current density was reduced immediately after the addition of potassium dichromates. Before the addition of 1000 ppm potassium dichromate, the measured maximum anodic current density was 0.04 mA/cm² (Figure 6.18 (a)), while it was reduced to 0.028 mA/cm² (Figure 6.18 (b)) immediately after the inhibitor addition. This behaviour is quite different from what shown in Figure 6.15. Meanwhile, the measured total anodic current density was also found to be reduced significantly immediately after the addition of potassium dichromate, as shown in Figure 6.19 (b).

When AA2024-T3 was exposed to 0.005 M sodium chloride solution for only 1 hour (Figure 5.12), fewer microcrevices were formed on AA2024-T3 surface comparing with that for 24 hours (Figure 5.27). In this case, it is much easier for dichromate ions to reach and passivate the entire aluminium surface. The passivation process could also result in an increase in anodic current density, but the dominating factor

should be the inhibition process, leading to decrease in anodic current density.

Figure 6.18 WBE maps of AA2024-T3 obtained (a) after 1 hr 0.005 M NaCl solution and (b) immediately, (c) 4 hrs, and (d) 24 hrs after the addition of 1000 ppm $K_2Cr_2O_7$ (WBE maps in a unit of mA/cm^2)

Figure 6.19 Changes of the (a) maximum and (b) total anodic current density with immersion time (AA2024-T3 in 0.005 M NaCl solution with addition of 1000 ppm $K_2Cr_2O_7$ after 1 hr exposure)

6.1.3 Anodic Polarisation Studies on the Corrosion Inhibiting Effects of Potassium Dichromate

WBE in conjunction with SRET measurements has been applied to monitor the changes of corrosion patterns and kinetics when AA1100 was under anodic polarisation. Figure 6.20 shows the pitting potential measurement of AA1100 in 0.5 M sodium chloride solution with and without 0.5 M potassium dichromate. With the presence of potassium dichromate, the pitting potential was approximately -650 mV vs. SCE, while the pitting potential of AA1100 in pure sodium chloride solution was approximately -760 mV vs. SCE.

Figure 6.20 Cyclic potentiodynamic polarisation of AA1100 in 0.5 M NaCl solution with and without 0.5M K₂Cr₂O₇

When the WBE specimen was exposed to a solution containing 0.5 M sodium chloride and 0.5 M potassium dichromate without any external polarisation, as shown in Figure 6.21 (a) and (b), corrosion occurred with anodic sites distributing over the WBE surface in a random manner. The corrosion behaviour was similar to that in Figure 5.1. Again, SRET was not able to detect currents flowing in the electrolytic phase over the WBE surface.

When the WBE was polarised to -611 mV, about 40 mV above its pitting potential, as shown in Figure 6.21 (c), anodic dissolution was accelerated with the maximum anodic dissolution current density increasing from 0.025 mA/cm² to 0.164 mA/cm². Meanwhile, the anodic dissolution sites remained almost unchanged.

(a) WBE map (free corrosion condition)

(b) SRET map (free corrosion condition)

(c) WBE map (immediately after polarised to -611 mV)

(d) SRET map (immediately after polarised to -611 mV)

(e) WBE map (30 mins after polarised to -611 mV)

(f) SRET map (30 mins after polarised to -611 mV)

Continued next page

Figure 6.21 (a) WBE and (b) SRET maps at open circuit potential, (c) WBE and (d) SRET maps immediately after anodically polarised to -611 mV, (e) WBE and (f) SRET maps for 30 min, and (g) WBE and (h) SRET maps for 1hr in 0.5 M NaCl $+0.5$ M $K_2Cr_2O_7$ solution (WBE maps in a unit of mA/cm^2)

However, when the duration of anodic polarisation was extended to 30 minutes and 1 hour, as shown in Figures 6.21 (e) to (h), major changes occurred to WBE and SRET maps. Major anodic dissolution sites, which were different from the major anodic sites in Figure 6.21 (c), were observable from both the WBE and SRET maps. Anodic dissolution currents increased significantly to a maximum value of 4.733 and later 5.346 mA/cm^2 . SRET measurements were able to detect anodic dissolution processes, as shown in Figures 6.21 (f) and (h), revealing similar anodic dissolution behaviour to that in the corresponding WBE map. When the maximum anodic currents measured using WBE increased from 4.733 mA/cm^2 to 5.346 mA/cm^2 , the maximum potential variations measured in corresponding SRET measurement changed from -0.25 mV to -0.75 mV. This result suggests another anodic dissolution mechanism - The formation of localised corrosion due to the formation of new localised anodic sites, which is different from the other localisation formation

mechanism i.e. localised corrosion initiates by minor anodes disappearing, that has been discussed in Section 5.1.3 (Page 84). This localised corrosion formation mechanism requires a higher anodic polarisation voltage and also an formation period, which appears to agree with conventional understanding on localised corrosion initiation due to polarisation of the materials above the pitting potential [Fontana 1981; Missert *et al.* 2002].

When polarisation voltage was removed and thus the aluminium WBE returned to free corrosion status, as shown in Figure 6.22, the WBE map became similar to that in Figure 6.21 (a), and SRET map became ‘empty’ again. The newly formed anodic dissolution sites in Figures 6.21 (g) and (h) ceased to exist. The mechanism behind this phenomenon is not clear and requires further investigation.

Figure 6.22 After removal of the anodic polarisation potential

This work suggests that, under polarisation conditions, SRET and WBE techniques were able to determine corrosion behaviour and profile below and above the pitting potential, and the effects of inhibitors.

6.2 Studies on Alternative Inhibitors to Dichromates

The WBE in conjunction with SRET method has been used to study corrosion inhibitors including lanthanide compounds and sodium molybdate, which have been developed as potential alternatives to dichromates.

6.2.1 The inhibiting Effects of Cerium Chloride

Figure 6.23 shows WBE and SRET maps obtained from AA1100 WBE surface in 0.5 M sodium chloride solution containing 1000 ppm cerium chloride. In such a solution, corrosion distributed in a random manner within the whole exposure period. Compared to AA1100 corrosion in pure sodium chloride solution (Figure 5.1), corrosion in the cerium containing solution was much more general. The number of anodes measured in cerium chloride containing solution was much larger than that in pure sodium chloride solution, as shown in Figure 6.24 (a). Furthermore, with the presence of cerium chloride, the localised corrosion intensity index of AA1100 became smaller, as shown in Figure 6.24 (b), indicating a more general corrosion behaviour. The measured maximum anodic current density was also reduced with the presence of cerium chloride. As shown in Figure 6.23, the largest measured anodic current density was only 0.011 mA/cm^2 . Again, SRET was not able to detect corrosion activities taking place in such a solution, as shown in Figure 6.23 (b).

The changes of maximum and total anodic current density are shown in Figure 6.25. It could be seen that even though the total anodic current density in the cerium containing solution was a bit higher than that in pure sodium chloride solution, the maximum anodic current density kept very small during the whole exposure period. It indicates that 1000 ppm cerium chloride was effective in inhibiting AA1100

corrosion in 0.5 M sodium chloride solution by reducing the tendency of localised corrosion.

Figure 6.23 (a) WBE and (b) SRET maps obtained after 1 hr, and WBE maps obtained after (c) 12 hrs, and (d) 48 hrs immersion in 0.5 M NaCl+1000 ppm CeCl₃ solution

(a)

(b)

Figure 6.24 Changes of the (a) number of anodes and (b) localised corrosion intensity index with the immersion time of aluminium AA1100 in 0.5 M NaCl solution with and without 1000 ppm CeCl_3

(a)

(b)

Figure 6.25 Comparison of the (a) maximum and (b) total anodic current density of AA1100 in 0.5 M NaCl solution and 0.5 M NaCl + 1000 ppm CeCl_3 solution

Figure 6.26 and Figure 6.27 show WBE and SRET maps obtained from AA2024-T3 WBE, which was exposed to a 0.005 M sodium chloride solution containing 1000 ppm cerium chloride and 100 ppm cerium chloride respectively. It could be seen that although many anodes existed on the WBE surface, the anodic current densities were very small. With the presence of cerium chloride, the largest measured anodic current density was only $8.461 \times 10^{-3} \text{ mA/cm}^2$, as shown in Figure 6.26 (c), while in pure sodium chloride solution the largest maximum anodic current density was 0.113 mA/cm^2 (Figure 5.11 (c)). The number of anodes measured in cerium chloride containing solution was much smaller than that in pure sodium chloride solution, as shown in Figure 6.28 (a). However, with the presence of cerium chloride, the localised corrosion index of AA2024-T3 fluctuated during the whole period of exposure, and remained smaller than that without any inhibitor, as shown in Figure 6.28 (b). Both the number of anodes and localised corrosion intensity index indicate that in the presence of cerium chloride, corrosion of AA2024-T3 in sodium chloride solution became more general. From Figures 6.27 and 6.28, it can be noted that even in 100 ppm cerium chloride containing solution, AA2024-T3 corrosion was also effectively inhibited. The 'empty' SRET maps, as shown in Figure 6.26 (d) and Figure 6.27 (b), indicate that SRET measurement was not able to monitor such corrosion process. The combined use of WBE and SRET has revealed the unreliability of SRET in the study of AA2024-T3 corrosion in cerium containing solution, while WBE was able to provide more information. This result can be used in further developing SRET technique, or at least it appeared to be useful to investigate in which corrosion system SRET can not be used and WBE has to be used.

The changes of maximum and total anodic current densities are shown in Figure 6.29. It could be clearly seen that the maximum anodic current densities were much smaller in the cerium chloride containing solutions (100 ppm and 1000 ppm) than

those in sodium chloride solution without any inhibitor, indicating that localised corrosion attack was reduced significantly in such solutions. The total anodic current densities were also found to be very small compared to those in pure sodium chloride solution, suggesting that general corrosion was also inhibited by cerium chloride.

Figure 6.26 WBE maps obtained after (a) 10 min, (b) 24 hrs, and (c) 48 hrs and (d) SRET maps obtained after 48 hrs immersion in 0.005 M NaCl + 1000 ppm CeCl_3

Figure 6.27 (a) WBE and (b) SRET maps obtained after 10 min immersion in 0.005 M NaCl + 100 ppm CeCl_3 solution

Figure 6.28 Changes of the (a) number of anodes and (b) localised corrosion intensity index with immersion time

Figure 6.29 Comparison of changes of the (a) maximum and (b) total anodic current density with immersion time in 0.005 M NaCl without any inhibitors, and 0.005 M NaCl containing 100 ppm and 1000 ppm CeCl₃ solution

It is interesting to note that there are initial current peaks on the total anodic current density curves of AA2024-T3 in cerium chloride containing solutions, as shown in Figure 6.29 (b), indicating fast anodic dissolution when the AA2024-T3 WBE was first exposed to cerium chloride containing solutions. Similar to the case of potassium dichromates, these initial current peaks should be due to oxidation reaction leading to passivation of AA2024-T3 surface.

From the total anodic current density curves in Figure 6.29, i_{inhi} can be obtained. The $IE_{Ce-1000}$ of 1000 ppm cerium chloride can be estimated using equation 6.4. i_0 (approximately 0.4332 mA/cm²) is the last measured total anodic current density in 0.005 M sodium chloride, and $i_{inhi-1000}$ (approximately 0.0297 mA/cm²) is the last measured total anodic current density in 0.005 M sodium chloride with 1000 ppm cerium chloride. Thus, the IE can be expressed as:

$$IE_{Ce-1000} = [(0.4332 - 0.0297) / 0.4332] \times 100 \approx 93.15$$

In 0.005 M sodium chloride and 100 ppm cerium chloride solution, the IE_{Ce-100} can also be estimated using equation 6.4, where $i_{inhi-100}$ is approximately 0.0089 mA/cm². Then, it gives

$$IE_{Ce-100} = [(0.4332 - 0.0089) / 0.4332] \times 100 \approx 97.94$$

The IE values of the 100 ppm and 1000 ppm cerium chloride containing solution are similar, indicating both concentrations of cerium chloride had similar efficiencies in inhibiting AA2024-T3 corrosion in 0.005 M sodium chloride solution. Hence, 100 ppm and 1000 ppm cerium chloride could be considered to be effective inhibitors for AA2024-T3 in 0.005 M sodium chloride solution. By comparing the IE values, corrosion patterns, it could be found that cerium chloride, an environmentally friendly compound, could be regarded as a promising ecological alternative to the conventional toxic inhibitor potassium dichromate.

Figure 6.30 shows WBE and SRET maps obtained from an AA2024-T3 WBE exposed to a solution containing 50 ppm cerium chloride and 0.005 M sodium chloride. Localised corrosion is clearly observable. Figure 6.31 shows the WBE and SRET maps obtained in 0.005 M sodium chloride and 10 ppm cerium chloride solution. It could be seen that corrosion behaviour of AA2024-T3 in such a solution was similar to that in 50 ppm cerium chloride containing solution. Corrosion of AA2024-T3 in 0.005 M sodium chloride solutions containing 50 ppm or less cerium chloride was much more serious than that in 0.005 M sodium chloride solutions containing 1000 ppm and 100 ppm cerium chloride. This result suggests that 100 ppm may be a minimum concentration for cerium chloride to effectively inhibit AA2024-T3 solution in 0.005 M sodium chloride solution.

Figure 6.30 WBE and SRET maps obtained after (a) and (b) 8 hrs, and (c) and (d) 48 hrs immersion in 0.005 M NaCl + 50 CeCl₃ solution

Figure 6.31 (a) WBE and (b) SRET map obtained after 2 hrs, and WBE maps after (c) 6 hrs and (d) 48 hrs immersion in 0.005 M NaCl + 10 ppm CeCl_3 solution

Figure 6.32 shows changes of the number of anodes and localised corrosion intensity index with the immersion time. It could be found that there were much less anodes on AA2024 specimen in the solution containing 10 ppm or 50 ppm cerium chloride than in the solution containing 1000 ppm cerium chloride. The localised corrosion intensity index has the smallest value in 1000 ppm cerium chloride containing solution, indicating the most general corrosion. In 50 ppm cerium chloride containing solution, the localised corrosion intensity index had the largest value, and performed an increasing trend with the exposure time, indicating corrosion became

more localised with the extension of corrosion exposure.

Changes of the maximum and total anodic current densities with immersion time are shown in Figure 6.33. It could be seen that in 50 ppm cerium chloride containing solution, the total anodic current density kept decreasing to a value similar to that in 100 ppm cerium chloride. After 48 hours immersion, the total anodic current density decreased from 0.07 mA/cm^2 to 0.023 mA/cm^2 , while that of 10 ppm cerium chloride decreased from 0.117 mA/cm^2 to 0.095 mA/cm^2 , which was much larger. However, it could also be noted that both the maximum and total anodic current densities were much smaller than that in pure sodium chloride solution.

Figure 6.32 Changes of the (a) number of anodes and (b) localised corrosion intensity index with immersion time of AA2024-T3 in 0.005 M NaCl solution with and without CeCl₃

(a)

(b)

Figure 6.33 Comparison of changes of the (a) maximum and (b) total anodic current density with immersion time of AA2024-T3 in 0.005 M NaCl solution with and without CeCl_3

IE of 50 ppm cerium chloride in 0.005 M NaCl solution can be estimated using equation 6.4. i_0 is 0.4332 mA/cm² (in 0.005 M sodium chloride solution without inhibitor); i_{inhi} here is approximately 0.0268 mA/cm² (with the presence of inhibitor). Thus, the **IE** can be calculated:

$$IE = [(0.4332 - 0.0268) / 0.4332] \times 100 \approx 93.70$$

That of 10 ppm cerium chloride containing solution can also be estimated using equation 6.4,

$$IE = [(0.4332 - 0.0947) / 0.4332] \times 100 \approx 78.13$$

The **IE** value of 10 ppm cerium chloride is much smaller than that of 100 ppm one, indicating 10 ppm is not a sufficient concentration for cerium chloride to inhibit AA2024-T3 in 0.005 M sodium chloride solution, whereas that of 50 ppm cerium chloride is similar to that of 100 ppm (**IE** = 97.94) and 1000 ppm (**IE** = 93.15). However, AA2024-T3 corrosion process revealed by WBE maps obtained from 50 ppm cerium chloride containing solution (Figure 6.30) is quite different from 100 ppm (Figure 6.27) and 1000 ppm cerium chloride (Figure 6.26) containing solutions. AA2024-T3 corrosion in 10 ppm and 50 ppm cerium chloride containing solutions was highly localised corrosion, whereas in 100 ppm and 1000 ppm containing solutions, AA2024-T3 corrosion was in general form. Thus, it could be concluded that corrosion protection, which is provided by 50 ppm cerium chloride for AA2024-T3 in 0.005 M sodium chloride solution, was actually not as efficient as that provided by 100 and 1000 ppm cerium chloride, because localised corrosion is much more damaging than general corrosion.

In another experiment, an AA2024-T3 WBE was immersed in 0.005 M sodium

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chloride solution for 24 hours, before 1000 ppm cerium chloride was added. Figure 6.34 shows WBE and SRET maps obtained before and after the addition of 1000 ppm cerium chloride. It can be seen that many new anodes appeared immediately after the addition of cerium chloride. Meanwhile, corrosion at some of the anodic sites, such as wire 61 and 89, intensified by the addition of cerium chloride, as shown in Figure 6.34 (c) and (e). The current density of wire 61 increased from 0.0393 mA/cm^2 (before the addition) to 0.1121 mA/cm^2 (after the addition), and that of wire 89 increased from 0.0691 mA/cm^2 (before the addition) to 0.1087 mA/cm^2 (after the addition). It illuminates that cerium chloride can intensify corrosion immediately after it was added into the corrosion system. Thus, it can be concluded that cerium chloride should be something other than a cathodic inhibitor, since cathodic inhibitors should never intensify corrosion. This result is quite different from conclusions suggested by other researchers [Davenport *et al.* 1991; Aldykewicz *et al.* 1995; Bethencourt *et al.* 1998]. They have considered cerium chloride as a cathodic inhibitor for the aluminium alloy AA2024-T3 in sodium chloride solution.

(a) WBE map (24hrs in 0.005 M NaCl)

(b) SRET map (24hrs in 0.005 M NaCl)

Continued next page

Figure 6.34 WBE and SRET maps obtained after (a) and (b) 24 hours immersion in 0.005 M NaCl solution, (c) and (d) 10 mins, and (e) and (f) 1 hr and (g) 12 hrs, and (h) 24 hrs immersion after 1000 ppm CeCl_3 was added into the 0.005 M NaCl (WBE maps in a unit of mA/cm^2)

Changes of the maximum and total anodic current densities are shown in Figure 6.35. It could be seen that there are marked increases in maximum and total anodic current densities immediately after the addition of cerium chloride. Similar to 1000 ppm potassium dichromate added at later stage of exposure (Figure 6.16), the increase of total anodic current density should be due to anodic reaction that leads to passivation of AA2024-T3 surface.

Figure 6.35 Changes of the (a) maximum and (b) total anodic current density with immersion time of AA2024-T3 in 0.005 M NaCl solution before and after the addition of 1000 ppm CeCl₃

The IE value can be estimated using i_0 that is obtained after 24 hours immersion in 0.005 M sodium chloride, and i_{inhi} that is the total anodic current density obtained after the addition of 1000 ppm cerium chloride for 24 hours. Thus, it gives

$$IE = [(0.4879 - 0.1053) / 0.4879] \times 100 \approx 78.42$$

This value is similar to that of potassium dichromates, when they are added at later stages of exposure ($IE = 81.89$, in Page 137).

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Another experiment was carried out by adding cerium chloride after AA2024-T3 WBE was immersed in 0.005 M sodium chloride solution for only 1 hour. Figure 6.36 shows the WBE results obtained before and after the addition of 1000 cerium chloride. It could be seen that the maximum current density measured immediately after the addition of cerium chloride was the same as that before the addition. Subsequently, the measured maximum anodic current density decreased gradually. However, the total anodic current density increased when cerium chloride was added in the sodium chloride solution, as shown in Figure 6.37.

Figure 6.36 WBE maps obtained (a) after 1 hr in 0.005 M NaCl solution, and (b) 10 mins, (c) 4 hrs, and (d) 24 hrs after the addition of 1000 ppm CeCl_3 (WBE maps in a unit of mA/cm^2)

Figure 6.37 Changes of the (a) maximum and (b) total anodic current density with immersion time

When the concentration of cerium chloride was increased to 2000 ppm, the WBE maps obtained before and after the inhibitor addition were different from those of 1000 ppm cerium chloride, as shown in Figure 6.38. It can be seen that the maximum current density decreased immediately after the addition of 2000 ppm cerium chloride. The measured total anodic current density also decreased, as shown in Figure 6.39.

When AA2024-T3 WBE was exposed to 0.005 M sodium chloride solution for 1 hour, localised corrosion of AA2024-T3 was much less serious than that for 24 hours. Thus, it is reasonable to expect that there were much less corrosion products that covered the WBE surface. In this case, it is easier for cerium ions to penetrate the corrosion products layer and reach the aluminium matrix. The passivation process can introduce large currents as discussed before, while inhibition process can reduce corrosion current density. Possibly, these two processes could occur simultaneously when cerium chloride was introduced into the electrolyte. The inhibition process involves the formation of cerium rich film at the cathodic sites reducing cathodic

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reactions significantly, and thus reducing the corrosion current density. In the case of 2000 ppm cerium chloride, corrosion current density reduced by the inhibition process could be a controlling factor, thus, the maximum and total anodic current densities were decreased.

In the case of inhibitor addition after 24 hours exposure, large amount of corrosion products may have formed, forming a barrier for cerium ions to reach the underneath aluminium. In such case, the formation of cerium rich film could be a slow process, and a partially protected surface could be responsible for a large anodic current.

Figure 6.38 WBE maps obtained (a) after 1 hr in 0.005 M NaCl solution, and (b) 10 mins, (c) 4 hrs, and (d) 24 hrs after the addition of 2000 ppm CeCl_3 (WBE maps in a unit of mA/cm^2)

Figure 6.39 Changes of the (a) maximum and (b) total anodic current density with immersion time

Cerium chloride was considered to inhibit aluminium corrosion by means of the formation of cerium-rich films preferentially over the cathodic precipitates, i.e. Al₆(MnFe). Such cerium-rich films were proposed to inhibit the cathodic reaction, and thus reduce the overall corrosion rate [Davenport *et al.* 1991; Aldykewicz Jr. *et al.* 1995; Bethencourt *et al.* 1998]. The cerium-rich film is considered to be easy to form on the cathodic particles because of the high local pH value around these particles. For these reasons, cerium chloride is considered as a cathodic inhibitor to AA2024-T3 by these researchers.

From the potentiodynamic polarisation curve of AA2024-T3 that has been carried out in 0.005 M sodium chloride and 100 ppm cerium chloride solution, as shown in Figure 6.40, it could be seen that with the presence of cerium chloride, the corrosion

current of AA2024-T3 electrode becomes much smaller. This suggests that cerium chloride has been efficient in inhibiting AA2024-T3 corrosion in 0.005 M sodium chloride solution.

Figure 6.40 Polarisation curve of AA2024-T3 in 0.005 M NaCl + 100 ppm CeCl_3

As discussed in Section 5.3 (Page 111 - 113), when S phase particles dealloy, pH increases locally at the periphery of S phase particles [Zhu and van Ooij 2003]. The pH can even increase up to 11 surrounding the S phase particles, as illustrated in Figure 2.3. The enrichment of OH^- around the S phase particles makes the cerium hydroxide easy to be formed at this area. Hence, the high pH environment can cause the formation of the so-called cerium-rich films, which mainly consists of the insoluble cerium hydroxide around the S phase particles. The cerium-rich films can

cover the S phase as well, and retard the anodic dissolution of S phase particles, and then impede the localised corrosion. Figure 6.41 schematically shows the mechanism by which cerium chloride retards further dealloying of S phase particles.

Based on the above analysis and the literatures [Davenport *et al.* 1991; Aldykewicz *et al.* 1995; Bethencourt *et al.* 1998], it can be concluded that cerium chloride may inhibit AA2024-T3 corrosion by forming insoluble cerium rich film – generally consists of cerium hydroxide/oxide [Hinton *et al.* 1986], on the dealloyed S phase particles, and the active cathodic particles as well. Thus, the mechanism by which cerium chloride inhibits AA2024-T3 in sodium chloride solution may be similar to the inhibitors which will inhibit both the anodic reactions and cathodic reactions.

Figure 6.41 Schematic illustration of the mechanism by which cerium chloride inhibit further dealloying of S phase particles in sodium chloride solution

SEM observation and EDS analysis show the evidence for this explanation. The SEM sample was prepared by adding 1000 ppm cerium chloride to 0.005 M sodium chloride solution after AA2024-T3 having been exposed to the electrolyte for one hour. SEM observation and EDS analysis were focused on the corroded area, which were usually dealloyed S phase particles, and the most cathodic particles – Al-Cu-Fe-Mn particles. The two particles shown in the Figure 6.42 were Al-Cu-Mg particles (S phase particles). It could be found that the large particle (particle A in Figure 6.42) consisted of less Al, and Mg, and more Cu, Ce, and O. This indicates that the dealloying of Mg and Al had started at the large S phase particle (particle A). The enrichment of Ce detected at the corroded S phase particle (Figure 6.42) indicates the formation of Ce-rich film on the dealloyed S phase particle. In addition, the enrichment of oxygen observed at this particle may be due to the formation of insoluble cerium hydroxide/oxide film. Such Ce-rich film could then inhibit further anodic dissolution at the S phase particle. It could also be found that the small particle (particle B in Figure 6.42) was plentiful of not only the elements of Cu, but also Mg, which indicates that little Mg was dealloyed and no severe corrosion taking place. Since there was nearly no corrosion occurring around this small particle, the pH value could not be increased to cause cathodic corrosion surrounding this particle. Hence, much less cerium could be observed around this particle because the pH value around this particle was not as high as that around the large particle.

Figure 6.42 SEM image and the elements mapping of Al, Cu, Mg, Ce, and O on AA2024-T3 after being immersed in 0.005 M NaCl solution for 1 hr

Particle shown in Figure 6.43 was Al-Cu-Fe-Mn containing intermetallic particle in AA2024-T3, which was exposed to 0.005 M sodium chloride solution for 1 hours before the addition of cerium chloride. From the element mapping, it could also be seen that cerium rich region was at the Al-Cu-Fe-Mn intermetallic particles, as shown in Figure 6.43 (CeL). The Al-Cu-Fe-Mn particle was generally considered to be effective cathodic site for corrosion of AA2024-T3 [Buchheit 1995; Obispo *et al.* 2000]. Thus, pH value could be high and lead to the formation of cerium-rich film. The enrichment of oxygen at this particle also indicates that this cerium-rich film may be mainly insoluble cerium hydroxide/oxide [Hinton *et al.* 1986].

Figure 6.43 SEM image and the elements mapping of Al, Cu, Fe, Mn, Ce, and O

In summary, cerium chloride was found to be effective in protecting AA2024-T3 from being corroded in sodium chloride solution. The inhibition efficiency of cerium chloride was dependent not only the concentrations of chlorine ions, but also the concentrations of cerium chloride. The mechanism of localised corrosion inhibition by cerium chloride may be something more than cathodic inhibition. Possible mechanism by which cerium chloride inhibits AA2024-T3 corrosion in sodium chloride solution may be the formation of cerium rich passive films on the entire AA2024-T3 surface, especially insoluble cerium hydroxide/oxide on both of

the anodic and cathodic sites.

6.2.2 The Inhibiting Effects of Lanthanum Chloride

As one of the environmentally friendly inhibitors, lanthanum chloride (LaCl_3) has also been studied using WBE and SRET in order to understand its corrosion inhibition performance and mechanisms. Various concentrations of lanthanum chloride have been used to inhibit AA2024-T3 corrosion in 0.005 M sodium chloride solution.

1000 ppm and 500 ppm lanthanum chloride were added to 0.005 M sodium chloride solution at the beginning of experiment. Figure 6.44 shows WBE and SRET maps obtained from an AA2024-T3 WBE surface exposed to 0.005 M sodium chloride solutions containing 1000 ppm lanthanum chloride. It can be seen that there were lots of anodes with very small current densities over the specimen surface. At the beginning of exposure, the current densities were in the range of $\mu\text{A}/\text{cm}^2$. The largest maximum anodic current density had a value of $0.015 \text{ mA}/\text{cm}^2$. No obvious anodic sites and cathodic sites can be observed on the SRET map, as shown in Figure 6.44 (b). When the concentration of lanthanum chloride was decreased to 500 ppm, much more severe corrosion could be detected by the WBE and SRET, as shown in Figure 6.45. The maximum anodic current density measured at the beginning of exposure was $0.04 \text{ mA}/\text{cm}^2$, which was much larger than that in 1000 ppm lanthanum chloride containing solution. The comparison of the number of anodes and localised corrosion intensity index of AA2024-T3 in sodium chloride solution with and without lanthanum chloride are shown in Figure 6.46. It can be seen that with the presence of 1000 ppm lanthanum chloride in the sodium chloride solution, corrosion became more general. Corrosion pattern in sodium chloride solution that contains 500 ppm lanthanum chloride appeared to be localised, which was similar to that in pure sodium chloride solution.

Figure 6.44 (a) WBE and (b) SRET maps obtained after 2 hrs, and WBE maps obtained after (c) 8 hrs, (d) 12 hrs, (e) 24 hrs, and (f) 48 hrs immersion in 0.005 M NaCl + 1000 ppm LaCl₃ solution

(a) WBE map: 2 hrs (mA/cm²)

(b) SRET map: 2 hrs

(c) WBE map: 8 hrs (mA/cm²) (d) WBE map: 12 hrs (mA/cm²) (e) WBE map: 24 hrs (mA/cm²) (f) WBE map: 48 hrs (mA/cm²)

Figure 6.45 (a) WBE and (b) SRET maps obtained after 2 hrs, and WBE maps obtained after (c) 8 hrs, (d) 12 hrs, (e) 24 hrs, and (f) 48 hrs immersion in 0.005 M NaCl + 500 ppm LaCl₃ solution

Figure 6.46 Changes of the (a) number of anodes and (b) localised corrosion intensity index with immersion time

Figure 6.47 shows changes of the maximum and total anodic current densities with the immersion time. It can be seen that both of the maximum and total anodic current densities decreased to low values after 48 hours immersion in sodium chloride solution containing 1000 ppm lanthanum chloride. By comparing the changes of maximum and total anodic current densities obtained with and without the presence of lanthanum chloride in sodium chloride solution, it can be seen clearly that lanthanum chloride was also an effective inhibitor for protecting AA2024-T3 in 0.005 M sodium chloride solution at the concentration of 1000 ppm, while the concentrations of 500 ppm was less efficient.

(a)

(b)

Figure 6.47 Comparison of the (a) maximum and (b) total anodic current density in 0.005 M NaCl solutions with and without LaCl_3

From the total anodic current density curves, the ***IE*** value of lanthanum chloride at various concentrations can be estimated using equation 6.4:

$$\mathbf{IE}_{La-1000} = [(0.4332 - 0.011) / 0.4332] \times 100 \approx 97.46$$

Where 0.4332 mA/cm² is the total anodic current density obtained after 48 hours immersion in 0.005 M sodium chloride solution, and 0.011 mA/cm² is the total anodic current density obtained after 48 hours immersion in 0.005 M sodium chloride solution containing 1000 ppm lanthanum chloride.

$$\mathbf{IE}_{La-500} = [(0.4332 - 0.0978) / 0.4332] \times 100 \approx 77.33$$

Where 0.0978 (mA/cm²) is the total anodic current density obtained in 500 ppm lanthanum chloride containing solutions.

The ***IE*** values of 1000 ppm lanthanum chloride, cerium chloride, and potassium dichromate are 97.46, 93.15, and 98.26 respectively, indicating that these three inhibitors have similar efficiency in inhibiting AA2024-T3 corrosion in 0.005 M sodium chloride solutions. However, potassium dichromate and cerium chloride have large ***IE*** values even at very low concentration, such as 100 ppm. At the concentration of 100 ppm, the ***IE*** value of potassium dichromate, ***IE*_{Cr-100}**, is 95.96, the ***IE*** value of cerium chloride, ***IE*_{Ce-100}**, is 97.94, while the ***IE*** value of 500 ppm lanthanum is only 77.33.

In another experiment, 1000 ppm lanthanum chloride was introduced after AA2024-T3 had been immersed in 0.005 M sodium chloride solution for 24 hours. AA2024-T3 specimen was further immersed in the lanthanum chloride containing solution for another 24 hours. This experiment was carried out for studying the

effectiveness of lanthanum chloride on inhibiting the localised corrosion of corroded AA2024-T3 surface.

WBE and SRET maps, as shown in Figure 6.48, show that with the addition of 1000 ppm at later stage of experiment, the corrosion pattern remained unchanged with stable anodes distributing randomly over the WBE surface. The maximum anodic current density was reduced from 0.096 mA/cm^2 (before the addition of lanthanum chloride) to 0.073 mA/cm^2 . With the addition of lanthanum chloride, the measured potential difference in SRET maps changed from -1.1 mV to -0.08 mV , indicating less intensive corrosion currents. After 24 hours, the major anodes were still existing, but with smaller current densities (0.04 mA/cm^2). From Figure 6.48 (e), it could be seen that only one major anode disappeared. This experiment demonstrates that the addition of 1000 ppm lanthanum chloride to the sodium chloride solution at later stages was unable to suppress all the existing anodes effectively.

Figures 6.49 shows the changes of maximum and total anodic current densities with immersion time. From the total anodic current density curve, the IE value can be estimated using equation 6.4

$$IE = [(0.4366 - 0.1412) / 0.4366] \times 100 \approx 67.66$$

Where 0.4366 mA/cm^2 is the total anodic current density over WBE surface after 24 hours exposure in 0.005 M sodium chloride solution, and 0.1412 mA/cm^2 is that after 24 hours exposure in 0.005 M sodium chloride with 1000 ppm lanthanum chloride present. This IE value indicates rather poor effectiveness of 1000 ppm lanthanum chloride as an inhibitor when it is added at later stages of corrosion exposure.

Figure 6.48 (a) WBE map and (b) SRET map obtained after 24 hours immersion in 0.005 M NaCl solution, (c) and (d) 10 mins, and (e) and (f) 24 hours after the addition of 1000 ppm LaCl_3 into the 0.005 M NaCl solution (WBE maps in a unit of mA/cm^2)

(a)

(b)

Figure 6.49 Changes of the (a) maximum and (b) total anodic current density with immersion time in 0.005 M NaCl solution with the addition of 1000 ppm LaCl_3

It could be seen that the maximum and total anodic curves of lanthanum chloride are quite different from those of 1000 ppm potassium dichromate (Figure 6.16) and cerium chloride (Figure 6.35). No significant increase in current density could be observed immediately after the addition of 1000 ppm lanthanum chloride into the sodium chloride solution. This indicates that lanthanum chloride may inhibit AA2024-T3 corrosion in sodium chloride solution by a different mechanism from that of potassium dichromate and cerium chloride. Since it never intensifies the corrosion process, lanthanum chloride should be a cathodic inhibitor for AA2024-T3 in sodium chloride solution.

6.2.3 The Inhibiting Effects of Sodium Molybdate

1000 ppm sodium molybdate was added at the beginning of corrosion exposure. The WBE and SRET maps show that severe localised corrosion occurred when AA2024-T3 was exposed to 0.005 M sodium chloride solution with 1000 ppm sodium molybdate, as shown in Figure 6.50. Very large maximum anodic current densities were detected by the WBE measurements. The maximum anodic currents were similar to those measured in the sodium chloride solution without any inhibitors. The maximum anodic current densities were found to keep increasing within the whole exposure period, Figure 6.50 (a) and (c). SRET measurements also detected large potential variations, as shown in Figure 6.50 (b) and (d), the potential variation was -0.25 mV after 1 hour immersion, and -0.47 mV after 48 hours immersion, indicating the enhancement of corrosion attack on AA2024-T3.

The WBE and SRET results obtained in this experiment demonstrate that sodium molybdate was not a suitable inhibitor for protecting AA2024-T3 from being corroded in sodium chloride solution. In the molybdate containing solution, some of the measured maximum anodic current densities were even higher than that in

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pure sodium chloride solution, as shown in Figure 6.51 (a), although, the total anodic current density was reduced slightly by the molybdate, as shown in Figure 6.51 (b).

Figure 6.50 AA2024-T3 (a) WBE and (b) SRET maps obtained after 1 hour and (c) WBE and (d) SRET maps obtained after 48 hours immersion in 0.005 M NaCl + 1000 ppm Na₂MoO₄ solution

The efficiency of 1000 ppm sodium molybdate in inhibiting AA2024-T3 corrosion in 0.005 M sodium chloride solution can be estimated using equation 6.4.

$$IE_{Mo-1000} = [(0.4332 - 0.3695) / 0.4332] \times 100 \approx 14.70$$

Where 0.4332 mA/cm² is the total anodic current density obtained after 48 hours immersion in 0.005 M sodium chloride solution, and 0.3695 mA/cm² is the total anodic current density obtained after 48 hours immersion in 0.005 M sodium chloride solution containing 1000 ppm sodium molybdate.

Compared with other inhibitors, i.e. potassium dichromate, cerium chloride, and lanthanum chloride, sodium molybdate performed the worst effectiveness at inhibiting AA2024-T3 in 0.005 M sodium chloride solution, as shown in Figure 6.51.

(a)

(b)

Figure 6.51 Comparison of changes of the (a) maximum and (b) total anodic current density with immersion time of AA2024-T3 in 0.005 M NaCl solutions with and without inhibitors

CHAPTER 7

Conclusions and Suggestions for Future Work

7.1 Concluding Remarks

This work has mainly explored the applications of the wire beam electrode (WBE) and scanning reference electrode technique (SRET) in study aluminium localised corrosion and its inhibition by various inhibitors.

The WBE method has been used to map current and potential distributions in the metallic phase, and the SRET has been used to map current or potential distribution in the electrolytic phase. In general, the WBE and SRET have been found to be useful for understanding the formation, propagation and the electrochemical behaviour of localised corrosion, and also its dependence on externally controllable variables such as solution pH, inhibitors and surface coatings. The combined use of WBE and SRET was found to be able to gain unique information on the process, kinetics and pattern of localised corrosion and its inhibition involving macro-scale separation of anodes and cathodes. Moreover, the combined use of WBE and SRET has revealed the unreliability of SRET in the studies of some corrosion system, while WBE appeared to be able to provide more information. It suggested that in some cases, SRET can be used since its specimen is easy to prepare; while in some cases WBE has to be utilised.

The WBE in combination with SRET method has been applied to study the corrosion processes of aluminium AA1100 in various corrosive environments. WBE measurements successfully revealed the changes of corrosion patterns of AA1100 in

sodium chloride solution at various concentrations, while SRET seemed not to be as effective as WBE in monitoring such changes. SRET appeared to be able to detect the corrosion patterns and pitting potential of AA1100 in neutral sodium chloride solution under anodic polarisation, which could introduce large anodic current. Localised corrosion intensity index, which was developed on the results obtained from WBE measurements, showed that corrosion of AA1100 was general at the very beginning of corrosion exposure, and became more localised at later stages of exposure. Both the WBE and SRET results revealed that corrosion of AA1100 became more severe with the presence of cupric ions in sodium chloride solution. It was also found that the mechanism of localised corrosion formation on AA1100 was associated with a process that minor anodes disappeared leading to accelerated dissolution of a few remaining anodes.

The combined application of WBE and SRET has been found to be a suitable method for studying localised corrosion and its inhibition of aluminium alloy AA2024-T3. Corrosion current distribution measured by the WBE measurement correlated well with the potential variation detected using the SRET, although the WBE measurement appeared to show more details of the corrosion process. The WBE was able to monitor the corrosion patterns of AA2024-T3 in sodium chloride solutions at various concentrations, whilst SRET was only able to detect the corrosion process taking place in sodium chloride solution at low concentrations. Corrosion kinetics of AA2024-T3 could also be evaluated by the WBE measurements, using the maximum and total anodic current densities as key parameters. It was also found that in sodium chloride solution, AA2024-T3 localised corrosion usually initiated by dealloying of the S phase particles, and followed by a synergetic process of dealloying, cathodic corrosion, and crevice corrosion. For Al-Cu-Fe-Mn containing intermetallic particles in AA2024-T3, corrosion was found to initiate by cathodic corrosion, followed by a synergetic process of cathodic corrosion, crevice corrosion. Galvanic corrosion, which was

Conclusions and Suggestions for Future Work

caused by the establishment of galvanic system between copper rich remnant (created by S phase dealloying) and aluminium matrix or the cathodic particle (Al-Cu-Fe-Mn particle) and aluminium matrix, was found to be a minor process.

Inhibitors including potassium dichromate, cerium chloride, lanthanum chloride, and sodium molybdate have been studied by exposing AA2024-T3 or AA1100 to sodium chloride solution. The inhibitors were introduced into the electrolyte either at the beginning of experiment or at the later stage of experiment. Potassium dichromates, cerium chlorides, and lanthanum chlorides have been found to protect AA2024-T3 from corrosion in sodium chloride solution. Efficiencies of these inhibitors depend not only on the concentration of inhibitors, but also on the concentration of chloride ions. Mechanism of different inhibitors was also studied by adding these chemicals into sodium chloride solution at the later stages of exposure. Potassium dichromate and cerium chloride behaved as an anodic inhibitor for aluminium corrosion in sodium chloride solution, while lanthanum chloride behaved as a cathodic inhibitor. Inhibition of AA2024-T3 corrosion in sodium chloride solution by cerium chloride was due to the formation of cerium rich passive films, especially insoluble cerium hydroxide/oxide on both the dealloying S phase particles (active anodic sites) and the active cathodic particles. The efficiencies of various inhibitors in protecting AA2024-T3 from localised corrosion were also estimated using the corrosion current densities measured by WBE. Cerium chloride was found to have a similar effectiveness to potassium dichromate at protecting AA2024-T3 in sodium chloride solution, while lanthanum chloride appeared to be less efficient. Sodium molybdate was found to have the poorest efficiency in inhibiting AA2024-T3 corrosion. It was also found that in the presence of inhibitors, corrosion pattern of AA2024-T3 in sodium chloride solution would generally change from the localised attack to a more general form.

7.2 Suggestions for Further Work

This research has raised some probabilities for further work.

WBE has shown its capabilities in investigating aluminium corrosion and its inhibitions by inhibitors. The inhibition efficiency of inhibitor can be estimate conveniently based on electrochemical parameters measured using the WBE. This method can be applied for further development of promising environmentally friendly alternatives, including both the organic and inorganic chemicals, in order to replace the conventional toxic inhibitor potassium dichromate. Mechanisms by which these future inhibitors protect aluminium and its various alloys may also be understood based on analysis of the maximum anodic current density, total anodic current density, and the number of anodes in WBE maps.

The WBE can also be applied to study new conversion coatings such as cerium based conversion coatings. For instance, the “self-healing” effects of chromate conversion coatings could be mimicked by investigating the release and migration of Ce(III) or Ce(IV) from cerium based conversion coatings. Figure 7.1 shows a possible experiment that can be used for the development of efficient conversion coatings for aluminium. An aluminium WBE can be prepared with cerium based conversion coatings covered on half of the working surface. Such a specimen can then be exposed to aggressive solutions and be monitored by means of the WBE. WBE measurements could contribute to better understanding of the performance and mechanism of the conversion coating system.

Figure 7.1 Schematic showing the investigation of cerium conversion coatings by means of WBE

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