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MICROELECTRODES IN Corrision Cracking

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Vasudev Rao

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By

VASUDEV RAO

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ABSTRACT

MICROELECTRODES IN CORROSION CRACKING

BY

VASUDEV RAO

Microelectrode technology has been developed by medical and biological workers for use in microanalytical and intracellular studies. The possibilities of applying this technology to investigations of corrosion phenomena are examined in this thesis.

pH microelectrodes with working tips rangimg from 10 to 30 micrometers diameter were developed for the study of corrosion mechanisms. Techniques for construction of stable microelectrodes, storage, calibration and use of these microelectrodes are described.

To study the conditions within a crevice, special experimental setups were developed, with which crevice corrosion conditions could be simulated and in which crevice width was adjustable.

Using microelectrodes with tip diameters 10 to 30 micrometers and working with AA 7075-T6 alloys, in a solution of 1 wt.% NaCl, it was observed that the pH in the vicinity of the crevice was most acidic and increased as the pH probe tip was moved towards the bulk solution.

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CHAPTER 1

INTRODUCTION.

1.1 GENERAL INTRODUCTION.

This thesis describes an experimental investigation of the electrochemical behavior inside an artificial crevice under unstressed conditions and in the presence of an aqueous chloride ion.

A major obstacle to a better understanding of the fundamentals of stress corrosion cracking has been the absence of information about the nature of the corrodent within a stress corrosion crack, particularly near the advancing edge. Although it is generally conceded that local chemistry within the stress corrosion crack differs considerably from that of the bulk solution, the demonstration has been deterred by inaccessibility and the problems of obtaining representative samples of the solution.

Because of the physical dimensions of the crack , pH electrodes cannot be used to determine the conditions existing within this crack. Hence, microelectrode technology has been used, the objective being to use electrodes with tip diameters less than one hundred micrometers.

In order to study the chemistry of the solution within a crack, a special experimental set-up was used, whereby an artificial crevice could be created. pH sensitive microelectrodes were fabricated in the laboratory and they were used to determine the pH of the solution within the crevice.

Generally, the results show the region of highest acidity was at the advancing edge of the crack with a gradual decrease in acidity in the direction of the bulk solution.

This thesis lays emphasis on the production of pH sensitive microelectrodes in the laboratory and their use in measuring the pH in an artificial crevice using AA7075-T6 specimens.

1.2 GENERAL BACKGROUND.

Aluminum owes much of its wide range of applications to its good corrosion resistance. However,high strength aluminum alloys,like all other alloys are subject to corrosion in chloride containing solutions. A better description of the solution inside the stress corrosion crack and the relationship between solution composition and crack growth is essential for understanding the stress corrosion cracking mechanism.

However, because of the physical dimensions of the crack, a quantitative analysis of the solutions inside these occluded cells has been proven to be a difficult task.

Although direct measurements are relatively easy for high strength steels and titanium alloys, in aluminum alloys the cracks are very narrow, and hence yield very small quantities of solution for analysis. Thus although it is possible to determine differences in pH between the solution at the crack tip and the bulk solution, the measurements for aluminum alloys are limited with regard to both accuracy and experimental versatility.

Davis[1] , working with AA7075 T6 alloys in a solution 4.4% Kcl in water at a pH of 5.8 to 6.2 and using microelectrodes with tip diameters 1 to 5 micrometers, observed that the pH in the vicinity of a crack tip was most acidic and increased as the pH probe tip was moved toward the bulk solution.

Rosenfield and Marshakov[2] constructed artificial crevices and investigated the factors affecting the mechanism of crevice corrosion. They observed that the pH within the crevice was more acidic than the bulk solution.

CHAPTER 2

THEORETICAL BACKGROUND

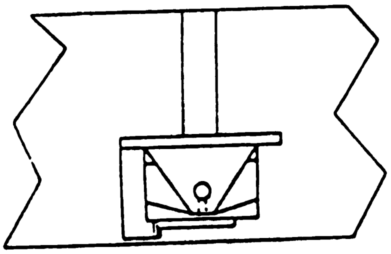
2.1 pH MICROELECTRODE.

The main attribute of the pH microelectrode is the smallness of its microtip. The pH microelectrode senses pH ($-\mathrm{Log}_{10}\ H^{+}$) as a potential difference which can be measured and recorded with the appropriate equipment. pH sensitive glass is a transducer, in that, it converts H^{+} from millimoles/litre to millivolts[3]. The parameters which determine the usability of the pH electrode are: size (tip diameter) and sensitivity (slope; millivolts/unit pH).

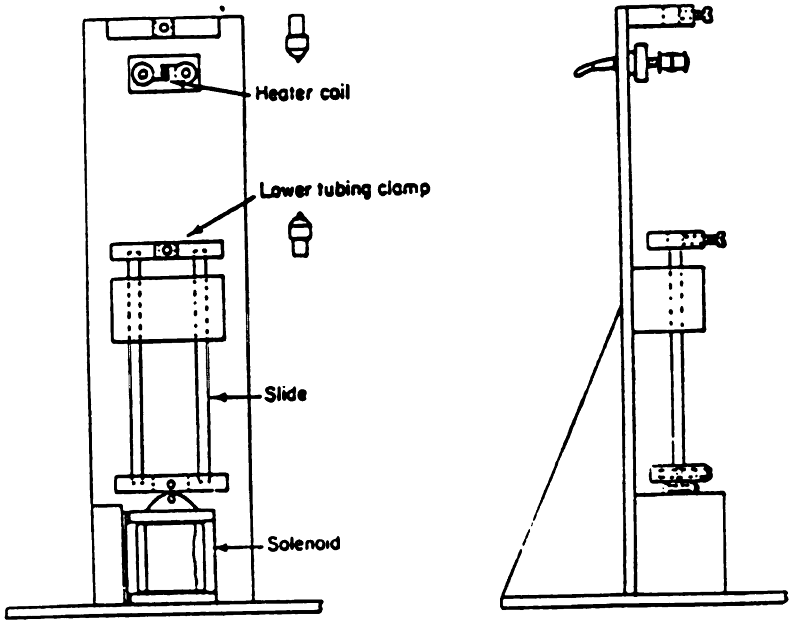
2.1.1 CONSTRUCTION OF MICROELECTRODES

A machine for making micropipettes is an essential tool in the construction of microelectrodes[4]. A vertical micropipette puller was used for this purpose. A schematic diagram of the micropipette puller is shown in Fig.1. The main parts of the micropipette puller are:

1] Vertical Back Plate
2] Upper Tubing Clamp



Top view



Front

Side

Fig. 1 Scale drawings of a vertical micropipette puller.

3] Lower Tubing Camp Attached on the Upper Crosspiece of the Slide

4] Heater Coils made of Kanthal Wire.

The vertical back plate is 33 cm high, 9 cm wide and 0.6 cm thick. The upper tubing clamp is mounted at the top and the lower clamp is on the upper crosspiece of the slide. The total free movement of the slide is about 6.5 cm. The holes for the tubing clamps are 8 mm in diameter. Glass tubings are held by pin vices fixed in the 8 mm holes. For conventional micropipettes the pin vices are removed and the glass is held by nylon screws which clamp the glass against nylon inserts mounted in the 8 mm holes. The heater coils are mounted on a block of insulating material which plugs into sockets in the back plate. The heater coils are made of Kanthal wire. Current for the heater coils is supplied by a variable transformer.

Production of optimally shaped micropipettes is very largely a matter of trial and error. According to Frank and Becker[5], the hotter and longer the heater coil, the longer are the micropipettes produced.

The micropipettes that are prepared by using a micropipette puller are then filled with 3M KCl solution by using a hypodermic needle[6,7]. Fine platinum wires or silver wires are then inserted in the tubing. A few pH microelectrodes have been prepared using silver-silver chloride inner components. A typical Ag-Agcl microelectrode is schematically shown in Fig.2[8].

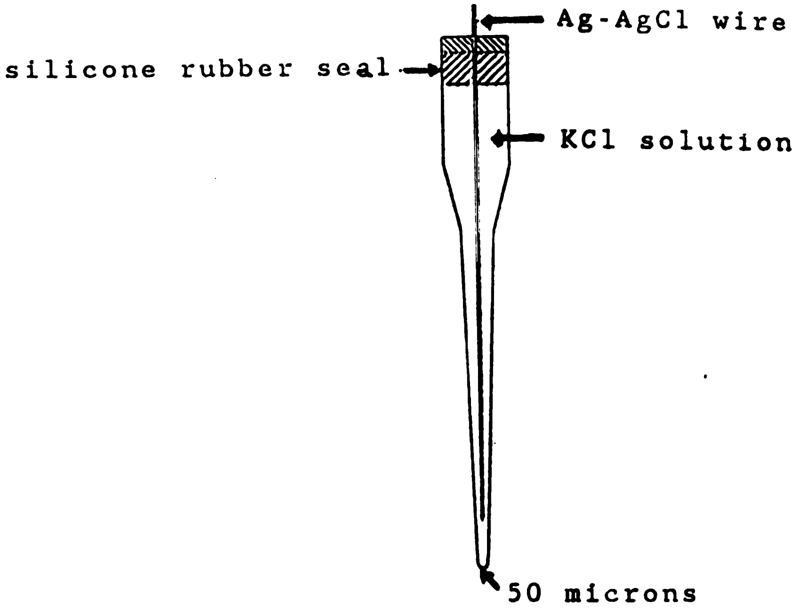


Fig. 2 pH microelectrode with silver-silver chloride inner components.

Since the potassium and chloride ions are very similar, it is believed that electrodes filled with concentrated KCl solutions have relatively small junction potentials. It is assumed that the 3M KCl electrode measures the resting potential without introducing a junction potential. Electrodes filled with KCl solutions have a high electrical conductivity and the junction potential is stable.

Silver-silver chloride microelectrodes were prepared by starting with a 10 cm length of clean 0.127 mm silver wire[9]. This was immersed for 8-10 min. in a solution of 10% NaCN - 5 % NaOH and etched to a fine point by applying a potential of 5V with the wire positive. The etched wire had the correct shape when the current has fallen to 50% of its initial value. About half of the etched portion is then chlorided electrolytically in dilute hydrochloric acid with a current of about 5 microamperes for 1 minute. The wire then is carefully positioned inside the borosilicate micropipette and temporarily secured using a fast-setting epoxy adhesive.

Preliminary measurements using pH electrodes with silver-silver chloride components indicate these to be superior to the preceding electrodes in terms of much less variation in potential readings with time[8]. This is illustrated in Fig.3, which includes results for microelectrodes constructed with chloridized silver wires.

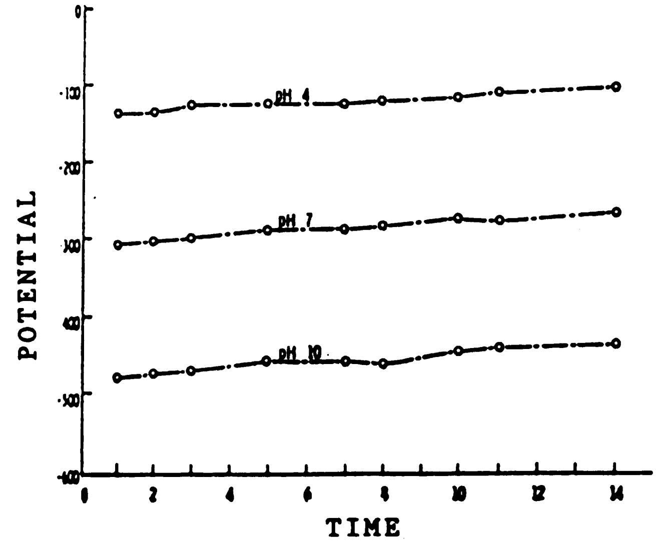


Fig. 3 Variation of potential with time of microelectrodes with silver-silver chloride inner components.

2.2 MEASUREMENT OF PH USING MICROELECTRODES.

The pH microelectrode senses pH as a potential difference which can be recorded using a Keithley electrometer Model 610 B[10]. A schematic diagram of Keithley Electrometer is shown in Fig.4. The Keithley electrometer Model 610 B is a versatile instrument which measures wide ranges of direct current voltages, currents and charges. It uses an electrometer tube input to provide greater than 10^{14} ohm input resistance.It consists of the following panel controls and terminals:

a) Range Switch

The range switch selects the measuring mode and the range. The electrometer has 11 voltage ranges from 0.001 volt full scale to 100 volts.

b) Multiplier Switch

The multiplier switch determines the voltage sensitivity of the direct current amplifier and sets the full scale range when the range switch is set to volts.

c) Meter Switch

The switch has five positions; **POWER OFF** shuts off the instrument. **OFF** disconnects only the meter during recorder operations. The + and - positions determine the

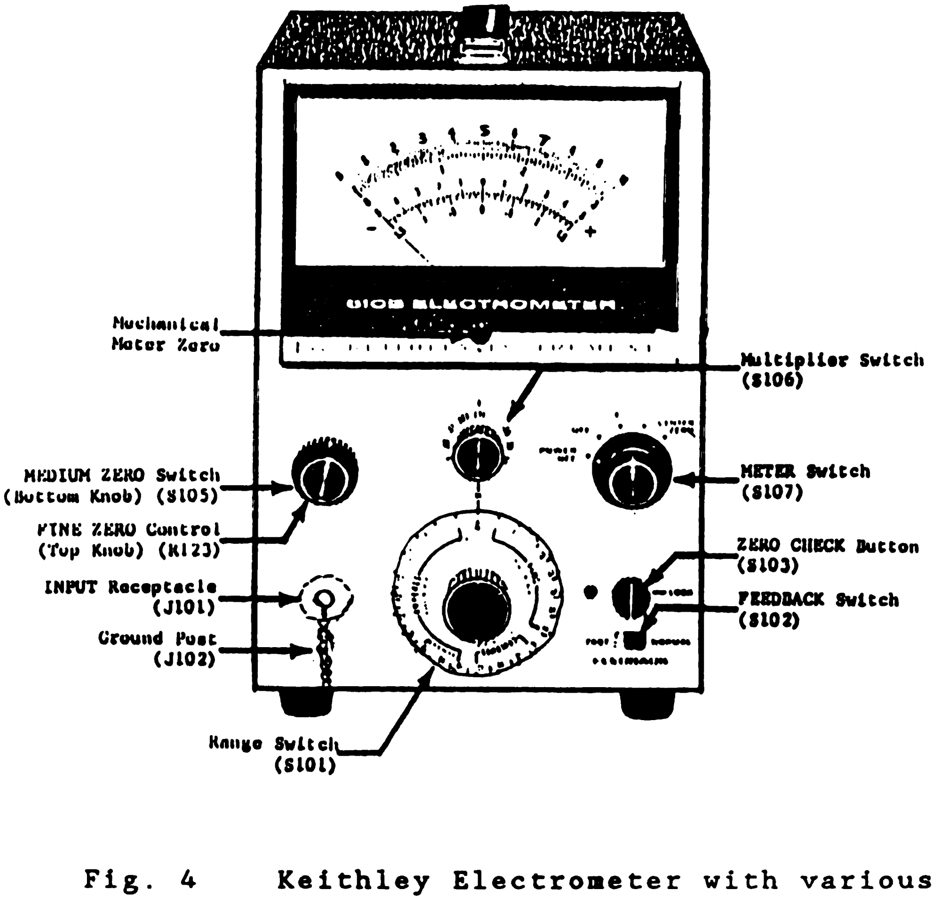


Fig. 4 Keithley Electrometer with various panel controls.

polarity of the meter. **CENTER ZERO** sets the instrument for center zero operation.

d) Zero Controls

Two zero controls are on the front panel; a **MEDIUM** switch (outer knob) and a 10 turn **FINE** potentiometer (center knob). These allow precise meter zeroing.

e)Input Receptacle

The **INPUT** receptacle is a Teflon-insulated uhf-type connector. A dust cap is provided. The ground post is below the receptacle.

f)Feedback Switch

The **FAST** and **NORMAL** positions of the switch determine the feedback connections within the instrument. Voltage measurements are made only in **NORMAL**.

g)Input Connections:

Using coaxial cables is the best way to make input connections. Carefully shield the input connection and the source being measured, since power line frequencies are well within the pass band of the electrometer. Unless the shielding is thorough, any alteration in the electrostatic field near the input circuiting will cause definite meter disturbances.

The Model 610 B's high input impedance allows circuit measurements without causing circuit leading.

2.3 CHEMISTRY OF THE SOLUTION WITHIN CREVICES.

The first attempt to analyze the solution at the crack tip in an aluminum alloy was made by Brown, et al[11]. They developed a freezing technique to contain the solution at the tip of a propagating crack in NaCl solution and found that the pH at the crack tip was acidic(pH = 3.5) and aluminum ions were present. Those findings were the first experimental confirmation of the prediction made by Edeleanu and Evans[12] that, after corrosion starts, the composition of the solution inside a pit or a crack should be different from that in the body of the solution. Referring to aluminum pitting, they concluded that due to imperfect mixing, the hydrogen ions accumulating within the pit must be equivalent to the hydroxyl ions accumulating outside the pit and the latter is responsible for the observed continued slow rise in pH in the body of the solution.

Rosenfield and Marshakov[2] constructed artificial crevices and measured corrosion currents that developed between otherwise equal electrodes, one in a crevice and the other with free access of electrolyte (0.5 N NaCl). A corrosion current of 160μ A/cm^2 developed with electrodes in the crevice functioning as the anode.

The solution in the crevice immediately became acidic and attained a pH of 3.2 to 3.4. They explained this value by the hydrolysis of Al^{+++} ion to give $Al(OH)^{++}$. From the hydrolysis constant of 1.4 x 10^{-5}, they calculated a pH of 3.5.

Studies by Sedricks et al[13] have supported the view that the propagation of intergranular stress corrosion cracks in Al-Zn-Mg alloys during exposure to aqueous chloride solutions occurs by anodic dissolution of the plastically deformed solid solution in the precipitate-free zones at grain boundaries. Thus it might be expected that those environmental factors which facilitate dissolution (e.g. lowering of pH) would facilitate cracking.

In acidic solutions the formation of a steady pH region of a stress corrosion crack in aluminum alloys is associated with the onset of aluminum hydroxide.

The extreme edge of the advancing crack is generally thought to be anodic to the rest of the specimen and thus is consumed in the corrodent by the electrochemical reaction

$$M \text{ --------------> } M^{z+} + Ze^-$$

where M is the metal in question and Z is the ionic charge involved.

Subsequent hydrolysis represented by the general equation

$$M^{z+} + x\,H_2O \text{ -----------> } M\,(OH)_x^{(z-x)} + x\,H^+$$

would produce an increase in acidity[11].

The specific electrochemical reactions taking place on metal surfaces in narrow recesses and crevices are primarily determined by the difficulty of transport of corrosive agents from the body of the elctrolyte to the metal surface in the crevice and the rate of removal of the electrochemical reaction products from the crevice. First of all, the extreme difficulty of oxygen access into the crevice alone creates a number of unique conditions for the anodic and cathodic reactions taking place in the crevice.

Increase in the rate of metal ionization reaction in the recess is due to the fact that, because of the lower oxygen concentration in the crevice, anodic metal dissolution takes place at more negative potentials. With a decrease in chloride concentration, the corrosion intensity in crevices decreases.

CHAPTER 3

EXPERIMENTAL PROCEDURE.

The experimental part of the work involved a two step procedure:

1) Fabrication,calibration and storage of microelectrodes.
2) Development of a special experimental set up to create an artificial crevice to study conditions within the crevice.

3.1 FABRICATION OF MICROELECTRODES

3.1.1 MATERIAL:

A borosilicate glass tubing with 1 mm outside diameter and 0.8 mm inside diameter was used in making micropipettes.

3.1.2 EQUIPMENT

A machine for making micropipettes is an essential tool in the construction of microelectrodes. A vertical micropipette puller was constructed in the laboratory with readily available materials. The heating coil was made of Kanthal A steel wire, which is very inexpensive and durable. The machine was operated as follows; the top end of a length of glass tubing was fixed in the upper clamp. The slide then was raised to the top of its range and the lower end of the glass tubing was fixed in the lower clamp. The upper and lower ends of the glass tubing were held by nylon screws which clamped the glass against nylon inserts mounted in the 8 mm holes. Then the heater current was switched on and the glass inside the coil began to soften. As the glass softened, the slide began descending under its own weight. The final pull of the slide produced two micropipettes.

3.1.3 FILLING OF MICROPIPETTES:

The micropipettes produced were filled with 3M KCl solution by using a hypodermic needle. The needle was inserted into the electrode which was held by hand and the electrolyte was injected by means of a syringe until most of the shaft was occupied by the fluid. While the hypodermic needle was being withdrawn, filling of the tip was completed.

3.1.4 PRODUCTION OF SILVER-SILVER CHLORIDE MICROELECTRODES:

Fine silver-silver chloride wires that were produced in the laboratory, wre then introduced into the borosilicate micropipettes and secured by using a drop of fast setting silicon rubber. The microelectrodes were then ready for use.

3.2 CALIBRATION OF MICROELECTRODES

The pH microelectrodes were conditioned by immersing the tips in distilled water for at least two hours before use. The electrodes were stored in distilled water before calibration measurements[8]. The microelectrodes were dipped in three standard buffer solutions and the potential readings were recorded using a Keithley electrometer. The silver portion of the silver-silver chloride electrode was connected to the high impedance input (+) of a Keithley electrometer Model 602, using a shielded cable with the shield connected to ground. The lowside [-] of the electrometer was connected to the test solution through a reference calomel electrode.

The tip of the electrode was immersed in three different buffer solutions and potential readings were recorded over a certain length of time. The calibration curve was obtained from the plot of pH versus potential.

3.3 SPECIMENS.

3.3.1 MATERIAL.

For all the measurements, bare rectangular sheets of high strength 7075- T6 aluminium alloys were employed. The chemical analysis and the mechanical properties of this aluminium alloy are given in TABLES 1 and 2[14].

TABLE 1[14]

CHEMICAL ANALYSIS OF AA 7075-T6

ELEMENT	Zn	Mg	Cu	Cr	Mn
Wt.%	5.52	2.76	1.41	0.23	0

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TABLE 2[14]

MECHANICAL PROPERTIES OF AA 7075-T6

	Tensile strength (psi)	Yield strength (psi)	Hardness (Rockwell)
Specimen	72,000	66,000	76 Rb
Handbook	83,000	73,000	85 Rb

3.3.2 SPECIMEN PREPARATION.

The working electrodes were mechanically polished up to 600 grit emery paper followed by cleaning in acetone, degreasing thoroughly in petroleum ether, the rinsing in distilled water and finally drying in air.

3.4 SOLUTION.

All solutions were prepared using distilled water just before each experiment. 1 weight % NaCl solution was used in the experiments. All the tests were conducted in unstirred solutions and at room temperatures.

3.5 EXPERIMENTAL SET-UP

An artificial crevice was created by using rectangular sheets of AA 7075-T6 alloys. The desired width between the metal test specimen was regulated by using polyethylene sheets between the metal specimens. This is shown schematically in fig.5.

The top side of the specimen was kept partially open for the insertion of the microelectrode, whereas, the other three sides were completely closed by gluing the specimens together.

The whole specimen assembly was immersed in 1 wt. % NaCl, including the tip of the electrode and potential readings were recorded on a Keithley electrometer. The specimens were immersed in the solution for three hours before the commencement of recording the potential within the crevice.

The silver portion of the microelectrode was connected to the high impedance input (+) of the Keithley electrometer and the low side (-) of the electrometer was connected through a reference calomel[15].

An artificial crevice of a depth of two inches from the surface was created and potential readings at different depths of the crevice were recorded. In order to simulate the conditions within a crack or device, the variation of potential from the crack tip to that of the bulk solution was recorded.

All potential readings reported are with reference to the saturated calomel electrode (SCE) as specified. The

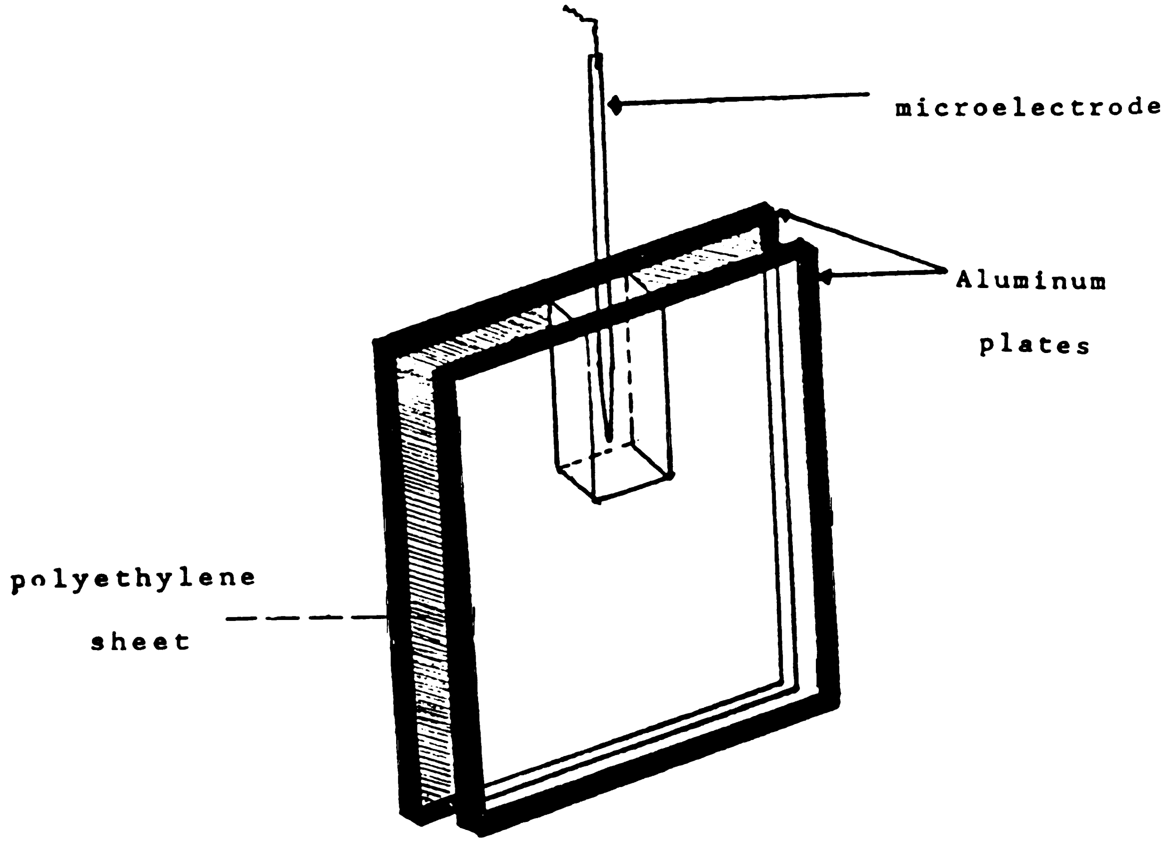

Fig. 5 Creation of an artificial crevice using aluminum plates.

potential readings at different depths of the crevice are shown in Table 3.

TABLE 3

VARIATION OF POTENTIAL WITH DEPTH OF PROBE TIP

DEPTH OF TIP (inches)	POTENTIAL (millivolts)
0.5	275
1.0	325
1.5	360
2.0	380

CHAPTER 4

RESULTS.

4.1 CALIBRATION RESULTS

The pH microelectrodes were conditioned by immersing the tips in distilled water for two hours before use. These electrodes were stored in distilled water between calibration measurements.

Fig. 6 gives potential readings in three standard buffer solutions over a period of time in electrodes with silver-silver chloride inner components. The results are for five probes possessing tip diameters of approximately thirty micrometers. The readings beyond seven days were obtained on all probes, but for the sake of clarity only one electrode was included.

Preliminary measuremente using silver-silver chloride inner components indicate these to be superior to the electrodes with platinum wire inner components in terms of much less variation in potential readings with time.

All of the measurements were obtained using a Keithley electrometer with a microelectrode tips immersed to a depth of 1/4 inch below the solution surface.

The slope of all satisfactorily functioning glass membrane pH microelectrodes, regardless of size,was very close to theoretical at 57-59 mV/pH unit at 22 C. Fig. 7

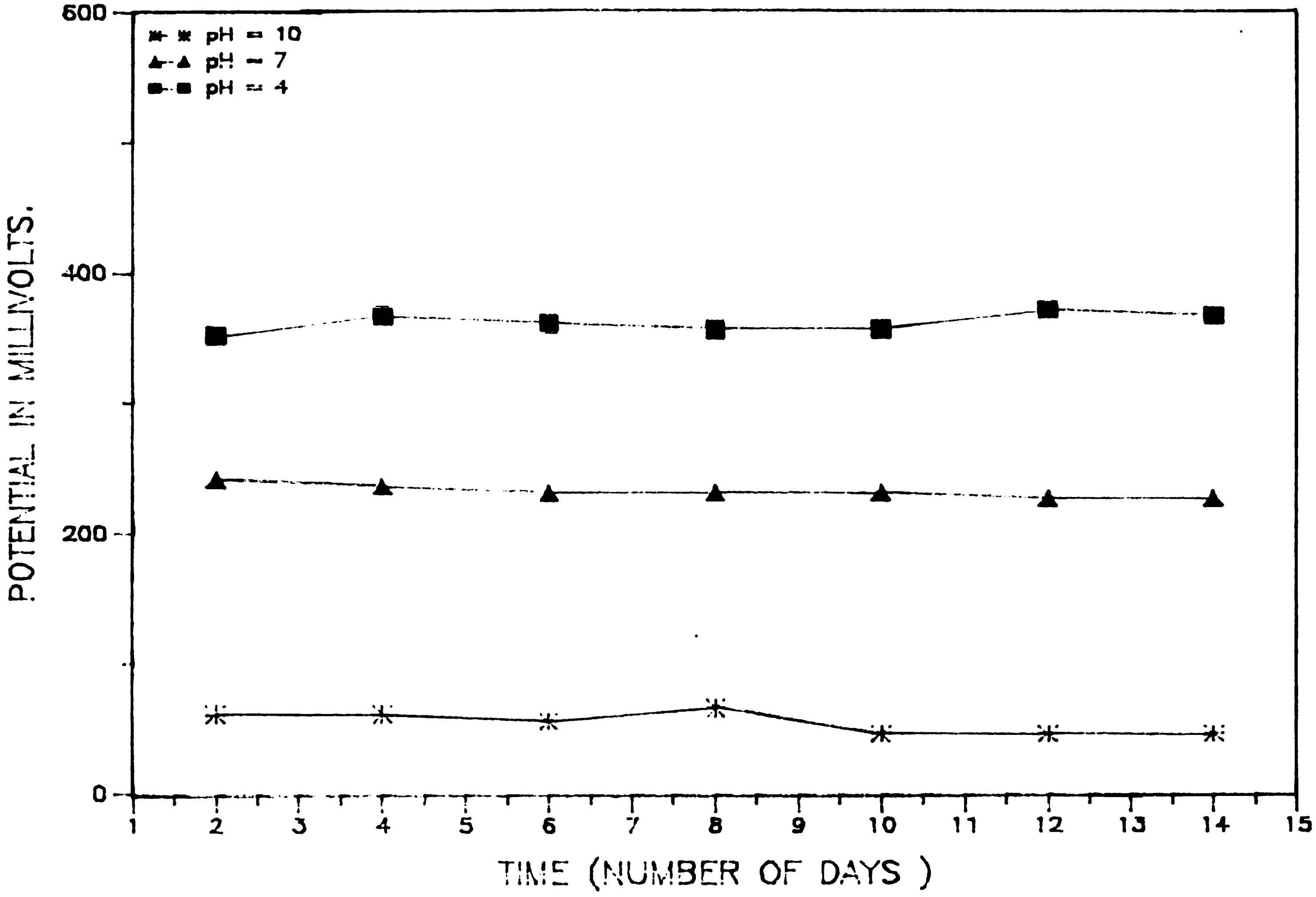

Fig. 6 Graphs showing the variation of potential with time in three standard buffer solutions.

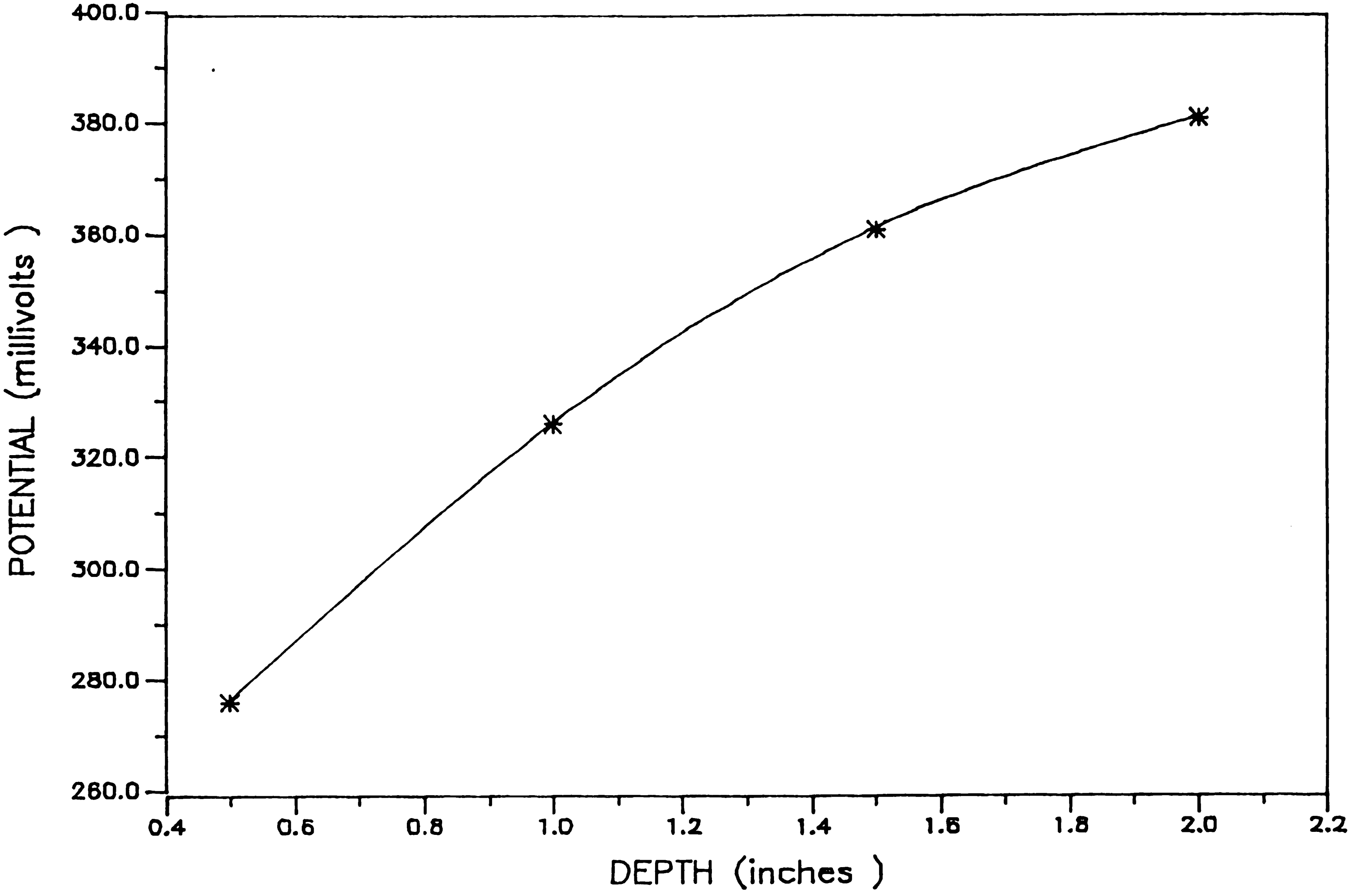

Fig. 7   Variation of potential with pH.

shows a plot of recorded voltage versus pH. This is the calibration curve for that particular pH microelectrode. The slope of an electrode was one of the criteria used to determine whether or not the tip was totally sealed and thus a satisfactorily functioning electrode. An electrode with less than 50 mV of slope was suspected of having an imperfect seal, a condition which could be verified with further testing.

Once the calibration curve was obtained, these microelectrodes could then be used to measure the pH of an unknown solution.

4.2 pH of the solution within the crevice

Initially, the pH of the bulk solution was determined using a pH meter. It was observed to be 6.85. As the tip of the microelectrode was lowered from the surface to about two inches within the crevice, it was observed that the solution within the crevice was more acidic than the bulk solution. The region of highest acidity was at the advancing edge of the crevice with a gradual decrease in acidity in the direction of the bulk solution. The pH of the solution within the crevice was more acidic and it was observed to vary from 3.8 to 4.2. The potential readings were taken over a period of time and with reference to saturated calomel electrode. There was a variation in potential with the depth of the tip of the microelectrode within the crevice. All potential readings were recorded on a Keithley electrometer and using the calibration curve, the pH within the crevice was determined.The variation of potential with the depth of the probe tip is shown in Fig. 8.

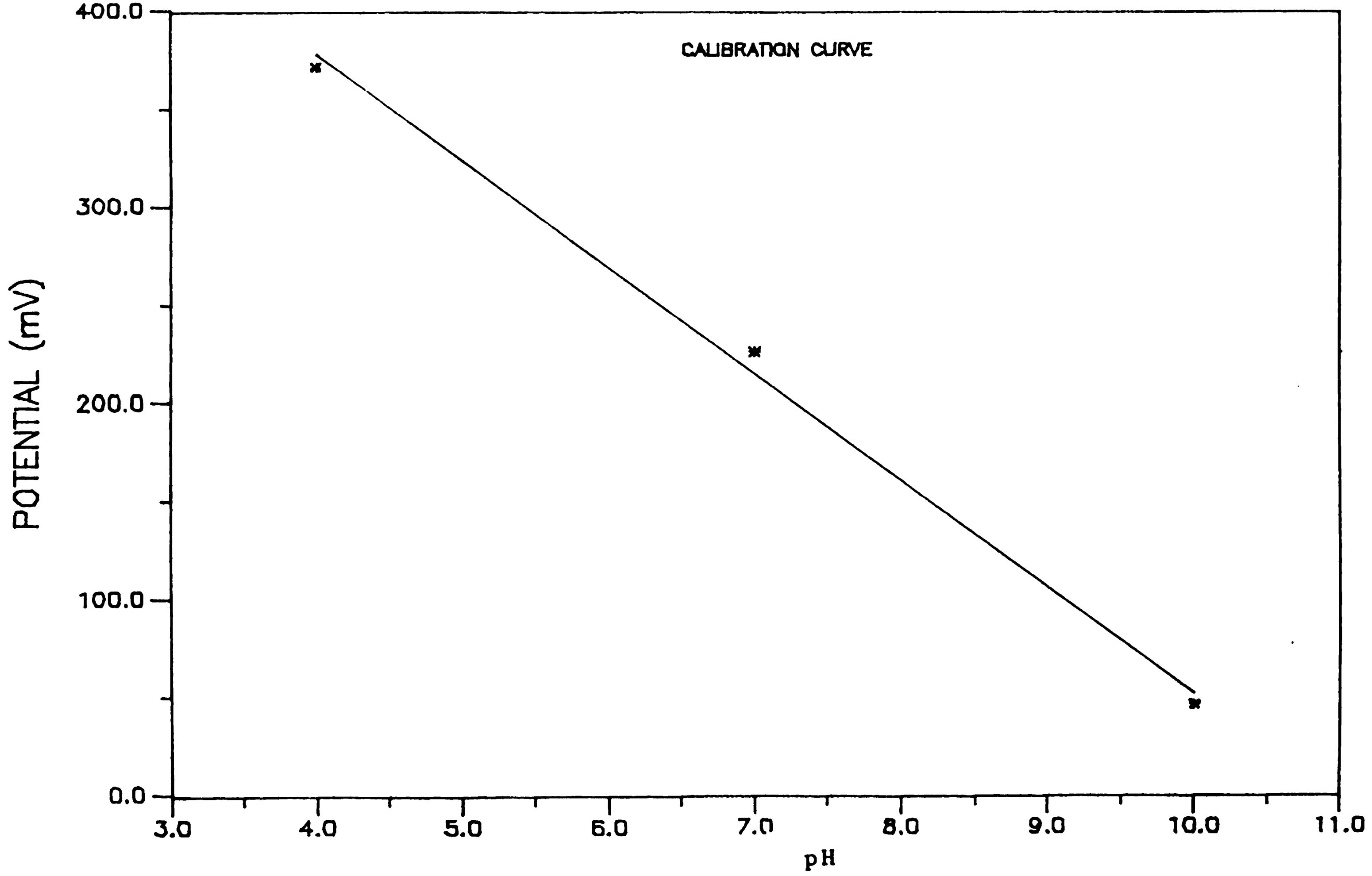

Fig. 8 A plot of potential versus depth of the micro-electrode tip.

CHAPTER 5

DISCUSSION

All test results indicate that the pH values determined by the special microelectrodes developed, were close to the theoretical values. It is felt that each one of the electrodes must be calibrated as carefully as possible before and after use.

The useful electrode lifetime seems to be about two weeks, after which irregular potentials develop and the electrodes are discarded.

The logical correlation of these results lies in the specificity of the anion. However, this specificity is not characterized in the same sense as it is in the classical corrosion literature that attributes to certain anions, such as the chloride ion, special properties, as the ability to penetrate oxide films or the ability to absorb at cracks. Rather, the significant specificity lies in the nature of the chemical species formed with the aluminum ion.

Scrape potential studies[16] have established the nature of transitory species formed when a bare, oxide free aluminum surface is exposed to an electrolyte as occurs at the advancing crack. Atomic aluminum is ionized to the hydrated aluminum ion, $Al(H_2O)_6{}^{+++}$ the reactions being

$$Al \dashrightarrow Al^{3+} + 3e^-$$

$$Al^{3+} + 3H_2O \dashrightarrow Al(OH)_3 + 3H^+$$

The surfaces inside the crevice are acting as non-aerated anodes where the metal undergoes corrosion and hydrolyzes with a decrease in pH.

$$Al(OH)_3 + 5H_2O + H^+ \dashrightarrow Al(H_2O)_6^{+++} + 2e^-$$

This ion $Al(H_2O)_6^{+++}$ is hydrolyzed rapidly to $Al(OH)^{+++}$. Whereas this complex ion is written $Al(OH)^{+++}$, it is assumed that it holds 5 water molecules, i.e. $Al(H_2O)_5OH^{++}$. This reaction and the resulting low pH have been described for solutions of all the common anions.[17]

$$Al^{+++} + H_2O \dashrightarrow H^+ + Al\,OH^{++}.$$

The subsequent reactions, that is, the reaction of the hydrated cation and the $Al(OH)^{++}$ species are dependent on the specific anion in solution.

When chloride is present, the reactions are:

$$Al^{+++} + Cl^{-} - Al\ Cl^{++} \text{ and}$$

$$Al\ (OH)^{++} + Cl^{-} - Al\ (OH)\ Cl^{+}$$

Within the occluded cell, the pH is low because of the hydrolysis and the Al^{+++} concentration builds up to 0.4M in chloride solution. The crack growth rate is high in chloride solution because of the formation of a transitory labile, aluminum chloride complexes.

In the absence of a specific anion reaction with the hydrated aluminum ion, the hydrated aluminum ion, the hyrolysis of the aluminum ion continues from $Al\ (OH)^{+++}$ to $Al\ (OH)_2^{+}$ and the dimer $Al_2(OH)_4^{++}$

The experimental result shows a decrease of pH inside the crevice and indicates weak acidity inside the crevice and chloride ion inside the crack affects the anodic dissolution.

Rosenfield[2] showed a general mechanism of real crack involving the effects of chloride ion and acidity.

$$Me + H_2O - 2e \text{ ---------}{>} MeO + 2H^{+}$$

$Me + H_2O - 2e \text{---------}{>} MeO + 2H^+$

$Me + 2(H_2O) \quad -2e \text{---------}{>} Me\ (OH)_2 \ + 2H^+$

$Me + 2\ Cl^- - 2e \text{---------}{>} Me\ Cl_2 + H_2\ O$

$Me\ Cl_2 + H_2 \quad O \text{---------}{>} MeO + 2H^+ + 2Cl^-$

It is believed that the manner in which chloride ion promotes pitting is caused by a defect structure set up where chloride ions exchange with oxygen ions on the Al_2O_3 lattice, electrical neutrality being maintained by the passage of an appropriate number of Al^{3+} ions from the oxide into the solution. At the higher chloride concentration the following reaction will take place:

$Al + 4\ Cl^- \text{---------}{>} Al\ Cl_4^- + 3e^-$

$Al + 4\ Cl^- + 3\ H^+ \text{---------}{>} Al\ Cl_4^- + 3/2 \ \ H_2$.

Generally speaking the crack growth rates can be correlated with the environmental factors by a consideration of specific aluminum anion complexes recalling also that the hydroxyl ion is an important anion in all of these aqueous solutions.

According to the results, the pH of the sulution in the crevice became more acidic as the tip of the microelectrode was moved towards the crevice.

CHAPTER 6

CONCLUSIONS

The following conclusions were drawn based on the experimental results:

1) pH microelectrodes have been sucessfully developed in the laboratory. These microelectrodes are capable of quantitative determinations of limited but useful accuracy. Presumably, they can be improved to the point where highly precise measurements on a microscopic scale will be possible in corroding systems.

2) A better description of the occluded cell associated with the cracking of AA 7075-T6 specimens in terms of composition has been developed. The composition, potential and crack growth can be related if it is assumed that the critical factor is the chemical reactivity of the aluminum anion complexes formed in the specific electrolytes.

3) The electrode potential at the tip of a corrosion crack which is growing by an anodic dissolution mechanism is lower than the bulk corrosion potential (i.e. the electrode potential at the crack tip is more active than at the crack mouth). Because of this effect, there are additional or alternative electrochemical reactions, such as hydrogen

evolution reaction as well as anodic dissolution within the crack.

4) There is a potential difference between the bulk and the crack tip. Because of this difference, the electrochemical force becomes more favorable for the development of corrosion inside the crack. Furthermore, enhanced anodic dissolution of the crack tip, together with the corrosion reactions at the crack surface, will result in compositional changes within the crack.

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