THE DETERMINATION OF pH, POTENTIAL AND CHLORIDE CONCENTRATION IN CORRODING CREVICES ON 304 STAINLESS STEEL AND 7475 ALUMINIUM ALLOY

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Abstract—The conditions in a simulated crevice have been studied for type 304 stainless steel and for 7475 T651 Al–Zn–Mg alloy in 0.6 M NaCl bulk solutions. The pH has been measured with a palladium/hydrogen diffusion electrode, and the chloride concentration with a silver/silver chloride electrode. For stainless steel the results conform with the expectations of the classical crevice corrosion model, with the crevice becoming a net anode, and the pH falling as a result of chromium ion hydrolysis. For the aluminium alloy more complex results are obtained, with parts of the crevice becoming mildly acidic (pH 3–4), while the deeper parts of the crevice become slightly alkaline (pH 8). The latter observation is not readily explained in terms of the chemistry and electrochemistry of the crevice.

INTRODUCTION

IT IS well known that the corrosion resistance of stainless steel and aluminium alloys is due to their ability to form a protective oxide film on the surface and become passive. A consequence of this otherwise admirable property is that these alloys are very prone to crevice attack because according to the general theory for crevice corrosion,¹ the passive film is broken down inside the cavity due to a decrease in local pH value. The determination of the solution chemistry and potential within these 'occluded cells' is essential, not only for evaluating crevice corrosion susceptibility. but also for understanding the mechanisms of pitting corrosion, stress corrosion cracking and corrosion fatigue of these alloys. Various workers have attempted to determine potential and/or solution pH values in crevices of stainless steel²⁻⁷ and in cracks and crevices of aluminium alloys⁸⁻¹², and a recent review has been made by Turnbull¹⁴. The simultaneous measurement of pH and potential in order to establish their correlation has received little attention. Recently, a technique was employed to study the crevice corrosion behavior of a high strength steel¹⁵ which illustrated that, under free corrosion potentials, these crevices were not subject to acidification and attack. This technique has been applied here to study the crevice corrosion of stainless steel and aluminium alloys under similar conditions.

The alloys examined were type 304 stainless steel (nominal composition 18% Cr, 8% Ni) and type 7475 aluminium alloy (4.7% Zn, 2.1% Mg). The electrolyte used in both cases was 0.6 M NaCl (pH 6).

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FIG. 1. The metal–Perspex artificial crevice assembly.

EXPERIMENTAL METHOD

Detailed descriptions of the crevice assembly and the measuring electrodes have been presented elsewhere^{15,16}. The artificial crevice was formed between a plate of the metal being studied, embedded in epoxy resin, and a Perspex (polymethylmethacrylate) electrode holder (Fig. 1a). The specimen/epoxy block was carefully surface ground to achieve a flat surface which was necessary in order to obtain a uniform crevice gap. This gap was controlled by the application of PTFE tape of the desired thickness between the specimen and the electrode holder. The crevices examined in this work were 8 cm long, 2.5 cm wide and had a gap of 90 \pm 10 μ m. The sample exposed in the occluded cell was coupled to a larger section of the same alloy (area ratios of 92:1 and 25:1 for stainless steel and aluminium, respectively), situated externally in the aerated bulk electrolyte and under free corrosion conditions, thus simulating an actual crevice corrosion situation.

The measuring electrodes were located in rows at 0.35, 1, 2, 4, and 7.5 cm from the crevice opening. Each of these measuring sites (configuration shown in Fig. 1b) contained a palladium foil electrode for the measurement of pH, an Ag/AgCl electrode for determination of chloride concentration and an agar/NaCl salt bridge leading to a saturated calomel electrode (SCE) which was used as a reference for the measurement of crevice potential. The salt bridge was located between the other two electrodes in each row so that minimum potential drops would be encountered during measurements.

The pH electrodes were constructed from palladium (99.99% pure) discs, 3 mm in diameter and 0.025 mm in thickness, which were spot welded to palladium wire for electrical connection, and mounted

 \mathbb{V}_{ϕ}

flush with the measuring surface of the electrode holder. The design of the pH electrode relied on the high solubility and the rapid diffusion of atomic hydrogen in the palladium lattice. As with the conventional platinum-hydrogen electrode, the pH-sensitive hydrogen redox equilibrium is established on the measuring surface of the palladium electrode, but here the electrolyte may be free from dissolved hydrogen. Instead, the atomic hydrogen required on the measuring surface is provided by maintaining hydrogen gas at one atmosphere in a small chamber at the rear of the electrode. Careful pretreatment and activation of the measuring surface was found to be essential for reproducible results.

The Ag/AgCl electrodes were prepared by chloridization of the cross-sectional surface of silver wires, 0.25 mm diameter, which were sealed with epoxy into the Perspex electrode holder.

The salt bridges were prepared by the addition of agar to 0.6 M NaCl solution, which was then heated. The hot mixture was injected in 0.63 mm outside diameter polythene tubing and allowed to set.

The surface of the crevice was pretreated by light abrasion with fine emery paper and degreased with acetone. The measuring electrodes were calibrated and the blocks were bolted together under the bulk electrolyte. Plastic nuts and bolts were used for this purpose. Two 20 l glass tanks were used to contain the bulk electrolyte. The crevice assembly was clamped horizontally in one tank with the plane of the crevice being just below and parallel to the bulk electrolyte surface. The external electrode, pretreated in a similar manner, was situated in the adjacent tank. The two tanks were coupled together with large diameter salt bridges. The temperature of the electrolyte was thermostatically controlled at $23 \pm 1^{\circ}$ C in both tanks. Agitation and aeration of the bulk electrolytes was achieved by the use of an air pump and glass frit bubblers.

The crevice metal and the external sample were coupled together after the crevice was formed and changes in solution pH value, potential and chloride concentration were monitored for about a week.

EXPERIMENTAL RESULTS AND DISCUSSION

Stainless steel

The variation of potential along the crevice with time is shown in Fig. 2 for the stainless steel sample, while Fig. 3 shows the variation of potential with distance from the crevice mouth. When the first readings were taken (about 5 min after assembly of the crevice had commenced), the free corrosion potential of the external alloy was



FIG. 2. The variation of potential along the artificial crevice of type 304 stainless steel with time in free corrosion.



Fig. 3. The variation of potential with distance from crevice mouth measured on the stainless steel.

-95 mV(SCE) and the corresponding values for the coupled crevice were more negative by 35-50 mV, depending on the distance from the crevice mouth. This indicated that the crevice was behaving anodically to the external material and hence was subject to dissolution. Subsequently, the external potential varied slowly with time, with the potential ranging from -125 to -75 mV(SCE), perhaps due to changes in the oxygen concentration of the bulk electrolyte. The crevice potentials fluctuated similarly, but the potential drops were decreased (to 6-9 mV) by the end of the experiment. The corresponding pH changes are shown in Fig. 4. The pH value in the crevice was lowered immediately after coupling and steady state values were attained after about 20 h. The final pH values were in the range of 1.7-2.7. The palladium foil at the 0.35 cm measuring site apparently came into contact with the crevice metal and hence no measurements were recorded at that site. This problem, which has been encountered on other occasions, is one of the limitations of the electrode, especially when it is employed in tight crevices. Nevertheless, the overall results appear to conform to the classical scheme of crevice corrosion of passive metals, in which the passive film in the crevice is destroyed due to local changes in chemistry and as a result active-passive galvanic cells are set up in which the localized attack on the relatively small surface area of crevice, crack or pit will be severe. The most acidic values were obtained at 2 cm from the opening, whilst the least acidic values were found at the site farthest from the crevice mouth. The observed minimum pH is presumably a result of the balance between diffusion to and from the bulk solution, which tends to raise the pH at the mouth of the crevice, and the current density distribution, which tends to give a lower pH value towards the mouth. The pH values obtained in this work were rather less acidic than those reported by Peterson³ (1.2-2.0) for the same steel but appear to fall in the range reported by Turnbull¹⁴ (0-3). A possible explanation for the rather high pH values observed is that the crevice gap was relatively wide compared to the very tight crevices which are



FIG. 4. The variation of pH along the artificial crevice of type 304 stainless steel with time in free corrosion.

generally found necessary to give severe crevice corrosion of austenitic stainless steel. The low pH values in the crevices of stainless steel, relative to those in carbon and low alloy steels, are due to the higher hydrolysis constants of the chromium ions and the significantly more positive external potentials on stainless steel.

The Ag/AgCl electrodes indicated insignificant changes in chloride concentrations from those associated with the bulk values. This was contrary to expectation and the findings of Mankowski and Szklarska–Smialowska¹⁷, who obtained large increases in chloride concentration in stainless steel pits. It is not clear why this result should have been obtained but it may indicate that significant complexation of chloride occurs in the crevice, and, although the concentration of chloride increases, the activity (which is measured by the Ag/AgCl electrode) does not.

Aluminium alloy

The potential measurements along the simulated crevice of the aluminium alloy (Figs 5–7) signified that after the initially low IR drops a steep increase in the potential drop occurred, with a potential difference of around 150 mV between the external surface and the crevice. This may have been partly due to an increase in the current flowing in the crevice, but bubbles (presumably of H₂) were observed to develop in the crevice at this time. The evolution of hydrogen from cracks⁹ and pits^{18,19} in aluminium has been reported previously. The appreciable reduction in the volume of the crevice electrolyte, due to these bubbles, may account for a significant rise in the resistance of the ionic path and hence would explain the large IR drops²⁰. However, the crevice remained anodic with respect to the external metal surface throughout the test. Dark patches, which increased in density near the crevice mouth, indicated that corrosion was indeed occurring on the crevice metal. The corresponding pH measurements (Fig. 7) indicated that whilst the pH value near the opening was acidic, those at the tip of the crevice had turned mildly alkaline.



FIG. 5. The variation of potential along the artificial crevice of aluminium alloy with time in free corrosion.



Fig. 6. The variation of potential with distance from crevice mouth measured on the aluminium alloy.



FIG. 7. The variation of pH along the artificial crevice of aluminium alloy with time in free corrosion.

The pH values of 3–4 observed near the mouth of the crevice are consistent with the results obtained by several workers for artificial crevices and stress corrosion cracks. Brown *et al.*⁸ obtained a pH of 3.5 in the stress corrosion cracks of 7075 Al alloy, while Sedricks²¹ performed macro-cell experiments in which the pH value in acidified chloride solutions containing fine Al turnings equilibrated at a value of about 4.5.

The evolution of hydrogen in the crevice is not surprising in view of the low potentials observed in the crevice, and the very active nature of aluminium metal. Because of the changes in local chemistry within the crevice the aluminium is no longer protected by a passive film, and the potential falls towards the equilibrium potential for aluminium dissolution. This is then assisted by the generation of hydrogen bubbles which increase the effective resistance of the crevice solution. The reasons for the pH value going alkaline in one part of the crevice, and acid in another are somewhat less obvious. It has been reported by Holroyd and Scamans¹³ that the pH in occluded cells in aluminium-zinc-magnesium alloys may become acid or alkaline, depending on the starting conditions and the presence or absence of an external surface. The aluminium occluded cell became alkaline when it was not coupled to an external surface. This is consistent with the findings of this work, in which the alkaline conditions were found in the deepest part of the crevice, where the effects of coupling with the external surface will have been least. While these findings are consistent with each other, and imply that an isolated aluminium-zincmagnesium alloy/seawater combination will give rise to alkaline conditions, the underlying electrochemistry and solution chemistry is unclear. In the absence of transport of dissolved species into or out of the crevice the most obvious net reaction is:

$$AI + 3H_2O \rightleftharpoons AI(OH)_3 + 1\frac{1}{2}H_2. \tag{1}$$

This may result in a small increase in pH, due to a slight solubility of the $Al(OH)_3$, but it seems somewhat improbable that this reaction could be responsible for the observed rise in pH. A possible explanation is that chloride-containing species are being formed, and as a result hydroxyl ions are being liberated according to a reaction similar to (2).

$$AI + 3H_2O + xCI^- \rightleftharpoons AI(OH)_{3-x}CI_x + 1\frac{1}{2}H_2 + xOH^-.$$
(2)

Nguyen *et al.*¹⁰ have also reported pH values of 7–9 in simulated crevices of 7075 Al alloy and they attributed it to the hydrolysis of Al^{3+} ions to $Al_2(OH)_4^{2+}$, which might be regarded as being similar to the effects of equation (2).

Another possible explanation (although it would not apply to the work of Holroyd and Scamans) is that the innermost site has behaved as a net cathode compared to some sites nearer the crevice mouth and there are some indications of this in the potential measurements. This suggests that the cathodic hydrogen evolution, or water reduction (leading to an increase in pH) occurred in the depth of the crevice, whilst metal dissolution and the subsequent hydrolysis (leading to a decrease in pH) was concentrated near the mouth of the crevice.

As in the stainless steel study, the potentials of the Ag/AgCl electrodes suggested that the chloride concentrations in the crevice remained unchanged at about 0.6 M. This result supports the findings of Nguyen *et al.*¹⁰ who observed no increase in chloride ions in their simulated crevice.

CONCLUSIONS

1. Crevice pH and potential values for crevices in type 304 austenitic stainless steel follow the classical pattern of crevice corrosion, with the crevice potential being more negative than the external potential, the crevice becoming acidified and corroding actively.

2. There are indications that, in contrast to expectations, the chloride activity in the crevice in 304 stainless steel does not increase during crevice corrosion. It is possible that this results from the rather wide crevice gap used in this work, or from complexation of the chloride leading to a reduced activity coefficient for chloride.

3. Crevice pH and potential values for crevices in 7475 aluminium alloy are consistent with previous work, although the crevice pH shows variable behaviour, going acidic near the crevice mouth, and alkaline in the deeper regions. The mechanism of the alkalization process remains uncertain.

4. There are indications that the activity of chloride in the crevice in 7475 aluminium alloy is not significantly different from that of the bulk solution. This is contrary to general expectations, although it is consistent with previous work.

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