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PITTING CORROSION BY BACTERIA ON CARBON STEEL, DETERMINED BY THE SCANNING VIBRATING ELECTRODE TECHNIQUE

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Abstract—The scanning vibrating electrode technique (SVET) has provided a non-destructive, on-line method for locating the presence and position of anodic electrochemical activity on the surface of carbon steel coupons. Using the SVET, changes in current densities over the steel with time were mapped in the presence and in the absence of bacteria. In a sterile liquid medium, the maps showed highly localized anodic current densities, which subsequently became inactive. Analysis of current maps and the open circuit potential (OCP) showed the potential transients were due to pit initiation and repassivation processes. When in the same bulk fluid, an aerobic bacterium, isolated from a corrosion tubercle, was grown, similar trends of pit initiation and repassivation were observed for several hours. However, after extended exposure to bacteria, local anodic activity did not repassivate. The corrosion then propagated and spread, until a large area of the sample was anodic. Recovery of the spent growth medium after growth of the bacteria, when used as the bulk solution, did not induce this irreversible pitting. These results indicated that the growth of bacteria altered surface conditions and prevented the initiated anodic sites from repassivating. The on-line non-destructive localized measurements possible by SVET can provide insight into the mechanisms of microbial influenced corrosion (MIC).

INTRODUCTION

THE ROLE of bacteria in metal corrosion in water is increasingly being considered as an important economic and environmental problem. Various mechanisms relating the activity of microbes and corrosion facilitation have been proposed. For example, the metabolic use of oxygen by non-uniformly colonized aerobic bacteria can lead to differential oxygen cells. Local cathodic depolarization by hydrogen consuming bacteria,[2,3] or anodic depolarization by iron reducing bacteria,[4] has been suggested to accelerate corrosion.

Measurement of corrosion influenced by bacteria, as well as evaluation of the above mechanisms has been difficult, due to the destructive nature of most corrosion measurement techniques. Direct current techniques require high applied currents, and therefore can alter biofilms.[5] Non-destructive techniques involving measurement of open circuit potential (OCP), linear polarizations, and electrochemical impedance spectroscopy (EIS) can provide on-line monitoring of corrosion rate, but provide the average corrosion rates for the coupon surface and only indirect indications of localized corrosion caused by MIC.[6]

The scanning vibrating electrode technique (SVET) provides a non-destructive

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means to define the magnitude and sign of current densities in solution over freely corroding metals.[7,8] Current density maps have been utilized to define localized anodic and cathodic activities of iron and stainless steel,[9] the galvanic corrosion of soldered copper,[10] and corrosion inhibition by phosphate and organic buffers.[11] In the present study, the SVET was used to detect localized corrosion of carbon steel in the presence and in the absence of an aerobic bacterium. The results showed that the SVET can be applied to MIC studies, as a non-destructive technique to determine local anodic and cathodic sites on-line.

EXPERIMENTAL METHOD

Bacteria and medium

Bacteria, used in this study, were isolated from a steel pipe tubercle.[12] The isolate has been identified as a *Pseudomonas* sp. based on the profile of membrane fatty acids. The isolate does not grow anaerobically, and does not produce detectable levels of volatile fatty acids when grown on glucose (1 g l^{-1}). The bacterium produces copious amounts of extracellular polysaccharide when attached to a steel surface, as revealed by Fourier transform infrared spectroscopy and by electron microscopy. These bacteria are commonly associated with biofilms, and can increase the corrosion rate of carbon steel, compared to sterile controls.[12] The medium used in these experiments was (in mg l^{-1} of glass distilled water) NH_4Cl 50, $MgSO_4 \cdot 2H_2O$ 50, $CaCl_2 \cdot 2H_2O$ 5, KH_2PO_4 27, glucose 50, 2-morpholinoethane sulfonic acid (MOPES buffer) 50, and trace minerals (in $\mu g\ l^{-1}$) $Na_2MoO_4 \cdot 2H_2O$ 0.1, $ZnSO_4 \cdot 7H_2O$ 50, $MnSO_4 \cdot H_2O$ 7.7, $CuSO_4 \cdot 5H_2O$ 2, $CoCl_2 \cdot H_2O$ 1, $NaB_4O_7 \cdot 10H_2O$ 0.8, $NiSO_4$ 0.5. This medium supports the growth of this bacterial culture.

Bacterial cells were grown to late exponential phase (24 h) in 100 ml of the medium described above. The cells were centrifuged and the spent medium was removed. The bacteria were resuspended in 100 ml of fresh medium. Fifteen ml of the suspension was added to the electrochemical cell.

Electrochemical cell

The working electrodes in these experiments were coupons of C1020 carbon steel supplied by Metal Samples (Munford, Alabama). The elemental composition of the steel from the supplier was given as, C 0.17, Mn 0.42, P 0.09, and S 0.006, wt%. The coupons were embedded in epoxy and finished with 600 grit silicon carbide. Thin, approximately 75 μm, pressure sensitive tape (3 M Co no 92) was used to insulate the sample except for an area in the center of the coupon approximately 25 mm^2 Microshield lacquer (Pyramid Plastics, Inc., Hope, Arkansas) was painted at the edge of the tape to reduce crevice corrosion. The cell had a working volume of 15 ml with a platinum wire for a counter electrode and a salt bridge to a saturated calomel reference electrode (SCE). The medium was aerated and stirred by air bubbling with filtered air.

Current density mapping

The vibrating electrode, used to scan the working electrode, consisted of an insulated platinum wire, 0.1 mm in diameter. The technique for current density mapping has been described elsewhere.[7,8] Briefly, the platinum wire was attached to a piezo-electric reed which was activated by applying a 200 Hz 10 V r.m.s. signal to the reed. The peak to peak vibration was 0.04 mm. The vibrating electrode was positioned at about 0.09 mm from the working electrode surface. The signal resulting from the vibration of the electrode in non-uniform potential fields was measured with a PAR model 116 lock-in amplifier. The signal from the lock-in amplifier was passed to a data acquisition unit and to a computer, where the data were analysed and plotted. The surface of the working electrode was scanned by moving the cell in 100 or 200 μm increments with computer controlled stepper motors. Scans were completed in less than 10 min, depending on the number of steps.

Polarization resistance

For determining polarization resistances (R_p), the potential of the working electrode was ramped ± 25 mV around the open circuit potential at a rate of 5 mV s^{-1}. Polarization resistance was determined by the slope of the potential versus current line.

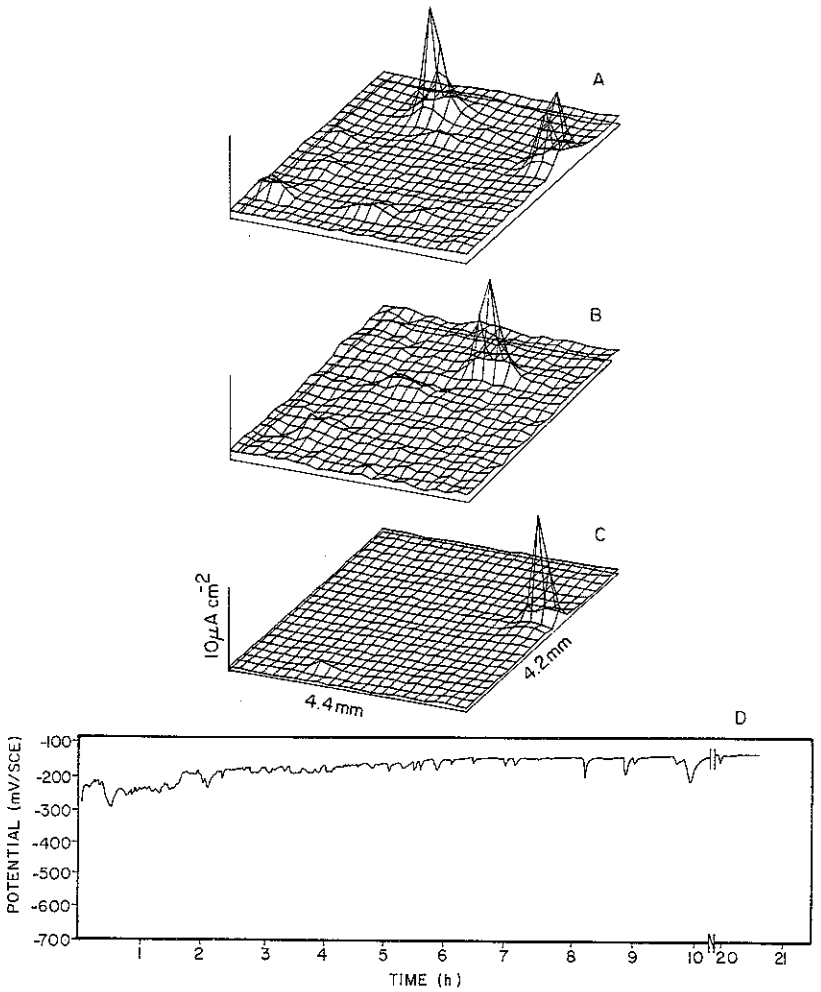

FIG. 1. Current density maps over carbon steel electrode in sterile aerobic microbiological medium. (A) 1 min; (B) 3 h; (C) 32 h; (D) open circuit potential for carbon steel in sterile medium. Vertical lines indicate times at which polarization resistance measurements were made.

EXPERIMENTAL RESULTS

OCP in sterile medium

In a previous study, investigating carbon steel corrosion in the same sterile medium used in this study, the OCP remained at approximately −200 mV(SCE) for the nine days of exposure.[12] In this study, the OCP was again monitored. Figure 1(d) shows the OCP versus time for the carbon steel in the sterile medium which was stirred by air bubbling. The OCP increased from an initial value of approximately −300 mV(SCE) to approximately −200 mV(SCE). The potential transients seen in Fig. 1(d) are characteristic of pit initiation followed by repassivation of the pits.[13]

SVET analysis in sterile medium

Current density maps over the carbon steel in the sterile air agitated medium are

shown in Fig. 1(a,b,c). Figure 1(a) shows five pits, which initiated immediately upon exposure of the metal to the medium. Figure 1(b) shows a single pit at a different location to the five seen in Fig. 1(a). The maximum anodic current density, 114 μA cm^{-2}, was observed after 25 min of exposure of the steel to the medium. This pit corresponds to a decrease in the OCP to approximately −300 mV(SCE) (Fig. 1d). This pit subsequently became inactive. Small pits, with measured current densities of less than 20 μA cm^{-2}, initiated at a different site. This sequence of pit initiation, repassivation and initiation at a different site occurred until the experiment was terminated after 32 h. Experiments involving current density mapping in sterile medium were performed twice, and similar results were obtained in both experiments. Measurement of OCP vs time in sterile medium were conducted six times, and similar trends to Fig. 1(d) were obtained.

OCP in inoculated medium

A comparison was made between pitting of the carbon steel in the sterile medium and medium containing a culture of an aerobic heterotrophic bacterium. The bacterial culture was prepared, as described in the experimental methods, and added to the electrochemical cell. As with the sterile medium, the inoculated medium was continuously bubbled with air. The OCP for this experiment is shown in Fig. 2(e). A trend similar to that observed for the sterile medium was observed for the first 4 h of exposure. The OCP, although lower than in the sterile control approximately −300 mV(SCE), shows pit initiation and repassivation. However, after six hours of exposure, the OCP slowly dropped, until it reached a value of approximately −600 mV(SCE) at 20 h.

SVET analysis in inoculated medium

The current density maps obtained for the inoculated system are shown in Fig. 2. After 5 h (Fig. 2a), two pits were observed. Although one of the pits becomes inactive, the more intensely dissolving pit continued to propagate (Fig. 2b). The anodic current density above the active pit and the area of the pit increased with time. The corrosion continued to propagate over the course of the experiment (Fig. 2c,d) until a large area of the coupon was anodic. Although the pit spread to the epoxy coating, the pit did not initiate at the coating.

The experiment containing bacteria was performed three times. Similar trends of pit initiation and repassivation followed by propagation and spreading of one pit was observed in all three experiments. The time required for a single pit to propagate and spread varied from 2 to 6 h for the three experiments.

Polarization resistances

The polarization resistance was measured by cycling the potential (5 mV s^{-1}) around the OCP (±25 mV). The times at which R_p was measured are indicated by the vertical lines in the OCP vs time diagram (Fig. 2e). The values of R_p for the sample exposed to inoculated medium were 4000 ohm cm^2 at 7 h, 2000 ohm cm^2 at 12 h, and 1100 ohm cm^2 for the 23 h measurement. In contrast to the sample, which contained bacteria, the sample which contained sterile medium gave a conventional value of R_p of 16,000 ohm cm^2 after 32 h of exposure. No active pitting was observed by SVET at the time of the polarization resistance analysis for the sterile control.

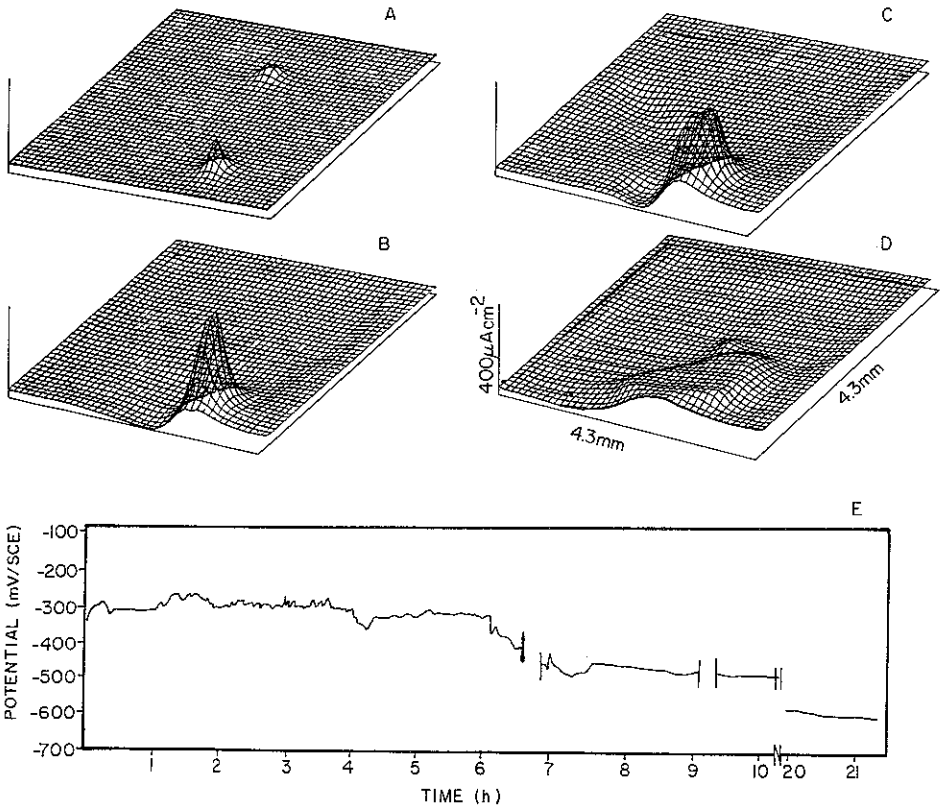

FIG. 2. Current density maps over carbon steel in inoculated aerated medium. (A) 3 h; (B) 7 h; (C) 11.5 h; (D) 23 h; (E) open circuit potential for carbon steel in aerated medium inoculated with bacteria.

OCP in spent growth medium

The composition of the electrolyte can greatly affect the corrosion of carbon steel.[11] Bacteria can alter the composition of the electrolyte, either by conversion of trace cations or anions into cellular material, or by the production of end products of metabolism, acids or alcohols. Corrosion of the carbon steel affected by changes in the medium due to bacteria, but with the bacteria removed from the medium, was determined. Bacteria were grown in the medium described above to late exponential phase (for 24 h). The bacteria were removed from the medium by centrifugation. The supernatant was then filter sterilized by passing the medium through a 0.2 μm membrane filter. The carbon steel was exposed to 15 ml of this filter sterilized spent medium. The measurement of OCP versus time showed a similar trend to that observed for sterile fresh medium (Fig. 3). The initial potential was approximately -300 mV(SCE), and the potential rose to approximately -200 mV(SCE) in the first hour of exposure. The OCP remained at this potential for the remainder of the experiment. The 'noisy' behavior, indicative of pit initiation and pit repassivation was also observed, although the frequency of the transients decreased. These results indicated that the changes in the medium due to bacterial activity, in the absence of bacteria, did not induce perpetuated pitting.

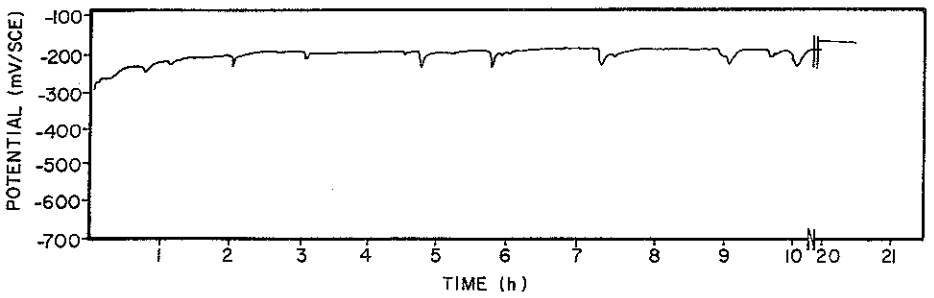

FIG. 3. Open circuit potential vs time for carbon steel electrode in spent aerated medium.

DISCUSSION

Pitting of carbon steel in sterile medium

The potential transients in this study were characteristic of pitting corrosion previously discussed.[9,13] For the short transients of a few minutes, the changes in potential were dominated by the capacitance of the passive surface. After pits initiated, the OCP dropped, and the capacitance of the passive surface was discharged producing the cathodic current equal to the anodic pitting current. If pits repassivated, then the OCP gradually rose. This rise is mainly associated with recharging of the passive surface. If pits continued to propagate, the OCP continued to drop. The cathodic current equivalent was then supplied by the slow oxygen reduction reaction. When the cathodic oxygen reduction reaction was sufficiently rapid, the rate of potential decrease slowed, and the contribution from capacitance discharge was negligible.[13]

The conditions in the sterile medium used in this study favored repassivation following pit initiation. The pit which gave the greatest magnitude of anodic current density, 114 μA cm^{-2}, which formed after approximately 0.5 h, corresponded to the lowest value of OCP, -300 mV(SCE) (Fig. 1). When the OCP rose to above -200 mV(SCE), no anodic current was observed over the area containing this pit. Smaller pits, with anodic current densities over the pit of less than 20 μA cm^{-2} were observed at different sites on the metal. These pits corresponded to drops in OCP of 20–70 mV.

The medium used in this study contained ionic species, as well as buffers, which are necessary for bacterial growth. The medium contained chloride, sulfate and phosphate ions at concentrations of approximately 1, 0.2 and 0.2 mM, respectively. Air was continuously bubbled through the media. An investigation has been carried out to determine the effect of medium components on the pitting of the steel under sterile conditions. It was shown that the presence of phosphate together with the aeration or stirring of the medium produced repassivation and inhibited propagating pits.[11]

Pitting of carbon steel in the presence of bacteria

In contrast, the presence or the metabolic activity, of aerobic heterotrophic bacteria had a marked effect on the corrosion of the carbon steel in a system containing the same medium. The OCP, rather than rising above -200 mV(SCE) as in the sterile control, slowly dropped to a value of less than -600 mV(SCE). The drop in OCP was not likely due to depletion of oxygen by bacterial respiration, since

the medium was continually bubbled with air. Bacterial growth was also limited by the supply of glucose, 0.28 mM. These conditions should not lead an anaerobic environment. The SVET analysis revealed that the drop in OCP corresponded to continued propagation of an initiated pit. Thus, the bacteria apparently altered conditions, which would normally lead to repassivation of pits. As these bacteria are biofilm producers, these films may act as membranes over areas where pits initiate. The membranes prevent solute losses from the concentrated solution within the pit or diffusion of hydroxyl or inhibiting ions from the surrounding solution.

Effect of spent medium

Since phosphate in the medium has been shown to inhibit corrosion in the sterile medium,[11] the consumption of phosphate by bacteria may have decreased this inhibition. In order to test this hypothesis, bacteria were first grown then removed from the medium. Pit propagation was still inhibited in this sterile spent medium (Fig. 3). These results suggest that pit propagation observed when bacteria were present was not due to phosphate consumption from the bulk fluid, nor from other changes in the composition of the medium. This conclusion is reasonable with respect to the glucose and phosphate concentrations in the medium. The concentration of glucose and phosphate were approximately the same, 0.28 mM glucose, 0.2 mM phosphate. The amount of glucose assimilated into cellular material is generally at least an order of magnitude greater than phosphate. Thus, with this limited supply of glucose, it is not likely that a high percentage of the phosphate would be utilized.

Polarization resistances

Polarization resistance is inversely related to the corrosion rate, as described by the Stern–Geary equation, which incorporates the anodic and cathodic contributions to the polarization resistance. The values for R_p presented here are in good agreement with earlier measurements containing this same medium and bacterium.[12] In the presence of bacteria, R_p ranged from 6000 ohm cm^2 at the onset of pitting to 1100 ohm cm^2 after the pit had propagated and spread, while sterile steel had a value of 16,000 ohm cm^2, when no pitting was apparent by the SVET.

Possible mechanisms of MIC

Organic acid production by anaerobic and facultately anaerobic bacteria has been proposed as a mechanism by which bacteria can increase the corrosion rate of metals.[14] In these experiments, the bacteria slightly lowered the pH of the medium, from 7.3 to 6.6. However, by removing the bacteria and testing in the spent medium demonstrated that this lowering of the pH, or other changes, in the bulk medium did not appear to significantly affect pitting with respect to sterile medium. The culture used in this study was a strictly aerobic bacterium, and did not produce detectable levels of volatile organic acids.[12] In addition, the medium used in this study was continuously aerated, which would prevent anaerobic conditions in the bulk medium, or development of a fermentative metabolism. Although acid production by bacteria in close association with the metal surface could not be excluded, these results suggest that acid production in the solution is not the major cause for the onset of corrosion facilitation.

Continued pit propagation requires the retention of aggressive ions and a low pH

inside the pits.[9] The dissolution current acts to increase the concentration of ions inside pits, and hydrolysis of ferrous ions maintains the low pH. In competition, diffusion from the pit reduces the concentration. Pit propagation is then a function of the ability to maintain a critical level of aggressive ions inside a pit.[9] Previous laboratory studies have demonstrated that the bacteria, used in this study, extensively colonized carbon steel coupons, and produced abundant extracellular polymer material.[12] Bacterial colonization of the metal may produce membranes that inhibit the diffusion of these aggressive ions from the pits. In addition, bacterial colonization of the surface may inhibit the diffusion of passivating ions, such as phosphate, from reaching the surface of the steel. These conditions could lead to the continued propagation of pits.

The results presented here demonstrate that the SVET and OCP in combination with detailed studies of *in situ* bacterial metabolic activities of specific bacteria can provide further insight into mechanisms of MIC, and can enhance clarification of the role of the constituents of the corrosion environment.

CONCLUSIONS

The scanning vibrating electrode technique can be used to obtain qualitative and quantitative information regarding localized corrosion influenced by bacteria. The results have shown that in complex sterile aerated medium containing millimolar concentrations of sulfate, chloride and phosphate, pit initiation is followed by their repassivation. However, when an aerobic heterotrophic bacterium is added to the medium, pits do not repassivate but continue to grow. The propagation of pits in the presence of bacteria resulted in a drop in the steel OCP and in the polarization resistance.

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