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TRANSITIONS IN ELECTROCHEMICAL NOISE DURING PITTING CORROSION OF ALUMINUM IN CHLORIDE ENVIRONMENTS

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ABSTRACT

Aluminum, in a chloride containing solutions close to its pitting potential, shows vigorous fluctuations in current and potential. Measurements have been made of the freely corroding potential, and the currents between interconnected electrodes. It is shown that there is a transition in the behavior of the transients. The transition occurs when multiple active pits are present and electrochemical communication occurs between them. The major source of current and potential transients is the growth process in the active pits rather than meta-stable pitting at the passive surface

INTRODUCTION

Aluminum and its alloys are susceptible to pitting corrosion in chloride environments. Fluctuations of potential and/or current are observed during the pitting processes [1-7]. These fluctuations are generally termed electrochemical noise. . Fluctuations has been increasingly studied [2-12] and related to a wide range of corrosion phenomena. The objective of many studies has been to derive the mechanisms involved in passivity breakdown and initiation of pitting. The processes taking place during pitting of stainless steel is understood than those of aluminum [6-12]; it is generally accepted for stainless steels that observed electrochemical transients are due to pit growth following an initiation process, and repassivation of metastable pits [7-12]. The open-circuit potential during metastable pitting of stainless steel in a NaCl solution shows a rapid drop, followed by a significantly slower rise to the original value. The current for pit growth is derived from the interfacial capacitance of the entire passive surface [8]. The slow recovery in potential after pit repassivation is thus due to recharging of the capacitance by the cathodic oxygen reduction reaction. The electrochemical transients with stainless steel below the pitting potential can be thus modeled as a consequence of superposition of these metastable pit events [2,9]. However, as shown in this communication, the electrochemical noise of aluminum in open circuit shows quite distinct features, thereby indicating that the basic mechanisms that control the pitting processes of aluminum are different from those of stainless steels. In what follows below, we demonstrate that the electrochemical transients during pitting of aluminum initially originates from processes similar to those on stainless steel but are then dominated by the electrochemical interaction between active pits once a number of pitting sites are active.

EXPERIMENTAL

Test specimens were fabricated from 99.9% purity Al wires (0.76 mm diameter) with cross sectional area of 4.5 x 10^{-3} cm^2 mounted in an epoxy resin. The surfaces of the specimens were wet-ground on 600 or 1200 grit silicon carbide abrasive papers and washed in distilled water. Solutions were made with analytical grade reagents and distilled water (18 MΩ). Samples surfaces were also covered with agar gel containing 0.05 M NaCl and a wide range pH indicator [14]. All measurements were made at room temperature.

Three electrode configurations were employed:

(i) A single-electrode specimen for an artificial-pit experiment. The artificial pit technique has been described previously [8,15]. Measurements were carried out using a potentiostat.

(ii) A double-electrode specimen. The centers of the electrodes were 1.0 mm apart. Open-circuit potential of the short-circuited coupled electrodes was measured against a saturated calomel reference electrode (SCE) with a high impedance (10^{13} Ω) electrometer (Keithley, model 614). The current passing between the coupled electrodes was also measured by another Keithley electrometer in the current mode. The outputs from these electrometers were fed to a 4 channel, 12 bit digital oscilloscope (Tektronix, TDS 420A) at an acquisition rate of 25 Hz.

(iii) A three-wire specimen. The currant flowing between the three Al wire electrodes cross sections was obtained by passing the currents to ground through three channels of the oscilloscope. The oscilloscope has internal 1 MΩ input impedances. Ohms law and the oscilloscope output voltage was used to determine the current distribution between the three electrodes.

RESULTS AND DISCUSSION

Figure 1 illustrates a 600 s trace of the current transients from the coupled double-electrode, and the corresponding open-circuit potential in 0.05 M NaCl. At the start of the measurement, the open-circuit potential increases from an initial value of –0.98 V(SCE) due to growth of the passivate film. Local currents flowing are the anodic passive oxide growth and the cathodic oxygen reduction. Following wet abrasion the local should be the same on each electrode but because of minor differences during abrasion washing, drying, and immersion in the 0.05 M NaCl, the two electrodes are not identical in either the growth of the passive film or catalysis of oxygen reduction. The current trace represents the difference in the net passivation and oxygen reduction currents of each electrode. One electrode shows a higher anodic passivation current that and is compensated by a higher oxygen reduction current on the other. These differences decay for about 50s when rapid events can then be seen superimposed on the slow current and potential changes. The potential curve starts to show intermittent rapid negative transients due to metastable pitting. The corresponding current transient is either positive or negative, depending on which electrode experienced pitting. After 300 s, the frequency and magnitude of the rapid potential and current fluctuations increase and the clearly defined potential baseline disappears as the potential begins to meanders by about 30mV around some imprecise value. This transition denotes a fundamental change in the corrosion process of the aluminum. Visualization measurements with agar gel containing a pH indicator demonstrated that there are only a few pits propagating at confined sites even when the vigorous fluctuations in current and potential commence [14,16]. It is suggested that, after the transition, the transients are not due to superposition of a number of metastable pit events, but are caused by the process occurring within a few active pits.

Details of a current and the open-circuit potential transient at 210 s before the transition are shown in Figure 2. The overall changes in the potential are similar in shape to those of the current curve. Each event displays a drop and a subsequent rise back to a potential baseline, and is accompanied by a current spike. These events are ascribed to pit growth and repassivation. The open-circuit potential of stainless steel generally shows smoother changes indicating distinct changes taking place. The kinetics of the repassivation of the aluminum is more complicated than those of austenitic stainless steel where the repassivation is almost immediate. The repassivation of stainless steel is followed by a local current process and recharging of the interfacial capacitance by the oxygen reduction reaction [8,9]. No currents would flow between interconnected electrodes [8]. With aluminum the interfacial capacitance is low and the recharging is expected to be more rapid. However, the results in Figure 2 show that the flow of current slowly decreases indicating the repassivation process is slow.

Figure 3 shows repetitive polarization curves of an artificial-pit electrode between –1.8 V(SCE) and 0.4 V(SCE) in 0.05 M NaCl at a sweep rate of 4.8 mV s^{-1}. Within the first few cycles of the polarization measurement, pits coalesce to form uniformly dissolving surface during the anodic regimes, which deepens as the experiment progresses. A roughly linear concentration gradient of metal ions along the geometrical occlusion is produced. An interesting phenomenon in Figure 3 is that a cathodic peak appears during the backward scan on each cycle. The amplitude of peak increases and the peak position shifts toward the cathodic direction as the measurement proceeds (as indicated by the arrow in the figure). These peaks are often ascribed to cathodic deposition of dissolved metal ions, presumably from impurities in the specimen. However, the results from high purity Al specimens (99.999%) also show similar cathodic peaks on the polarization curves. Thus it is unlikely that these peaks are due to the presence of impurity ions.

It is most likely that these are attributed to cathodic reduction of hydrogen ions. The following reaction occurs at the anodic site:

$$Al = Al^{3+} + 3e^- \tag{1}$$

Local acidification is followed through hydrolysis

$$Al^{3+} + H_2O = Al(OH)^{2+} + H^+ \tag{2}$$
$$Al(OH)^{2+} + H_2O = Al(OH)_2{}^+ + H^+ \tag{3}$$
$$Al(OH)_2{}^+ + H_2O = Al(OH)_3 + H^+ \tag{4}$$

Inside the pit an increase of hydrogen ions must be accompanied by an increase of metal ions, thereby decreasing local pH. The reduction of hydrogen ions to hydrogen gas

$$2H^+ + 2e^- = H_2 \tag{5}$$

dominates and produces a cathodic polarization immediately after the rapid dissolution of aluminum stops. The concentration of H^+ remains higher for longer periods with an increase in the geometrical recession of the dissolving surface because a diffusional distance between the metal/electrolyte interface and the bulk solution becomes longer. As a consequence, the cathodic peak rises with increasing measurement cycle. Assuming that all the charge during the anodic polarization is expended for metal dissolution, the calculated pit depths are 0.012 mm, 0.048 mm, 0.084 mm, 0.12 mm, and 0.156 mm for 1st, 2nd, 7th, 10th, and 13th cycles, respectively. It is most likely that the pronounced cathodic current is provided by the hydrogen production reaction inside the pit when anodic dissolution takes place. Because hydrogen evolution is fairly rapid in acids, the fast potential recovery for Al pitting (Figure 2) can be attributed to this cathodic reaction. Note also that the impedance of hydrogen ion reduction reaction derived from the of the current/voltage slopes (Figure 3) at the open circuit potential around –800mV, is lower than the corresponding (2 $M\Omega.cm^2$) polarization resistance of the original passive surface by two orders of magnitude. Direct polarization measurements of active pits have also been carried using vibrating electrode techniques and have shown that cathodic currents can be drawn from the active pits [7].

Current transients flowing between three electrodes in agar gel containing 0.05 M NaCl and a pH indicator are shown in Figure 4. The development of pH changes in solution at sites on the electrodes were observed with a video camera and recorded on a videocassette. At the onset of the measurements, the anodic current increase from electrode 3 correlates with almost identical cathodic currents supplied by electrodes 1 and 2. This indicates that anodic pitting dissolution commenced on electrode 3 and cathodic current was supplied from oxygen reduction at almost identical passive surfaces of electrodes 1 and 2. The sum of all three observed currents is close to zero. (The pitting current is probably three times the current observed on either electrode 1 or 2 because the local current from the passive surface of electrode 3 would also produce the same cathodic current). The appearance of a single low pH site at on electrode 1 confirms that only one pit was active. At 150 s the current from electrode 2 starts to rise indicating that a pit was growing on electrode 2. Concomitantly the currents to the other two electrodes decrease. It is essential to note that the decrease in current from electrode 3 is much greater than that from electrode 1 which characterizes the behavior of the passive surface. Between 150 s to 188 s. the current from electrode 3 decreases by 37 nA while that from electrode 1 the decreases by only 9 nA. It is apparent that the response of electrode 3, with the growing pit, is considerably greater than the response of electrode 1, with an intact passive surface when the new pit on electrode 2 is formed. This demonstrates an easier communication between pits than with the passive surface because of the lower effective impedance of the pits. pH changes again indicate a second active pit on electrode 2.

The following rationale for the results may be proposed: when a single pit propagates on an electrode surface; the corresponding cathodic current is supplied by (i) oxygen reduction on the passive surface (ii) hydrogen ion reduction inside the pit, and (iii) the passive film capacitance. The current transient measured when two electrodes are used and only one pit is present, is thus determined by reaction (i) and (iii). In other words, the electrochemical transients are dominated by the reactions between a pit and the passive film. When pits propagate at two electrodes the observed system response is thoroughly altered. The impedance of active pits is much lower than that of the passive film and the pits then interact with each other. The anodic dissolution and cathodic hydrogen reduction occur within and/or between the pits. The reactions on the passive film no longer dominate the characteristics of the observed transients. The complex patterns of the electrochemical transients after the transition result from the competitive process between the active pits. Extrapolating the expected behavior to larger surfaces is a function of the number of active pits and the area of the passive surface. Either other pits or the passive surface depending on which has the lower impedance will dominate the response to a transient.

The shape of current transients from both electrodes 1 and 2 correspond closely to the shapes of the corrosion potential transients at times prior to 160s suggesting the responses were due to changes taking place on electrode 3. Only one pit was seen on electrode 3 suggesting that a single pit on this electrode was producing all the transients. In principle visually unobservable metastable pits, because of their short duration, could also contribute to the currents from electrode 3. However, then similar transients must be expected from other passive surfaces on electrodes 1 and 2. Such events were not discernable from the currents or potential. This leads to the proposition that the transients prior to 160 s were virtually all caused by processes within a single growing pit on electrode 3. Hence we conclude that the dominant transient processes reflects the electrochemistry within growing pits, rather than metastable pitting events on the general passive surface. Tunneling [see ref 1 p. 136] takes place intermittently at extreemly high rates [17] and can produce the observed transients associated with pitting. The correspondence between the shape of the potential variations and the currents from electrodes 1 and 2 is indicative of a linear polarization resistance of the passive surface.

At times greater than 160 s, after the transition, the magnitude of the transients increase. The current from electrode 1 is the sum of the large fluctuation in current from electrodes 2 and 3. The currents from electrode 1 continues to correspond closely to the potential indicating a passive surface with virtually no metastable pitting events. There is a major interaction between electrodes 2 and 3 mirroring changes in their behavior. Visual observations show both electrode 2 and 3 now have low pH sites corresponding to active pits. The cause of the larger transient is a result of decreased system impedance brought about the formation of the second active pit. The increase in the frequency of the transients is a result of the sum of the changes taking place in both pits. The changes in chemistry in pits can then markedly affect the corrosion potential and produce the potential meandering of about 30 mV. The masking the characteristics of the oxygen reduction reaction on the passive surface which continues to take place in the background. The in open circuit potential of the polarization curve in Figure 3 when the potential is being decreased are due to changes in concentrated in $AlCl_3$ and changes in the kinetics of reaction taking place in the pit. Changes in the open circuit potential or zero current from pits observed during local current density polarization measurements were also shown to vary with time by 50 mV [7].

CONCLUSIONS

A transition in behavior of the electrochemical transients results when there is a change in the dominant electrochemical paths of the current. Before the transition, transients are dominated by oxygen reduction at the passive surface and to some degree by the passive film capacitance. These transients result probably from metastable pitting events. After the transition aluminum shows vigorous fluctuations in current and potential. The transients are then dominated by the growth processes in the pits and not to metastable breakdown of the passive surface. The magnitude of the fluctuation increase because of the increased number of pits and a reduced impedance of the system. The low impedance of the pits produces a complex patterns of transients after the transition. The characteristic slow meandering of the median corrosion potential with aluminum is caused by the chemical variations within active pits.

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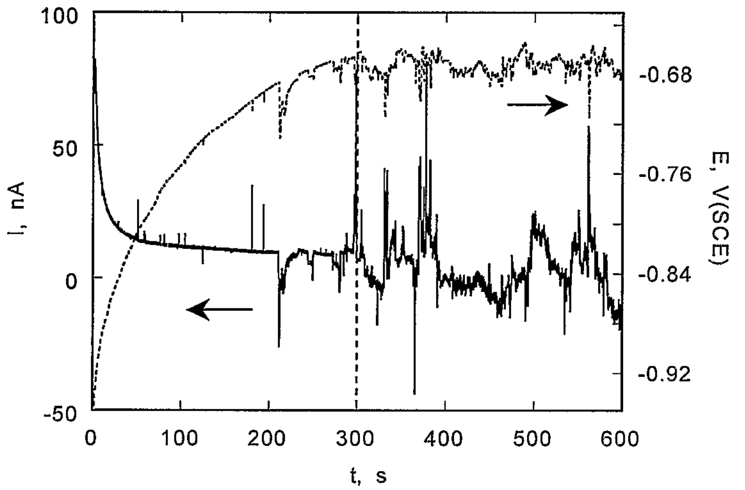

Figure 1. Open-circuit potential variations and the current between two coupled Al electrodes in 0.05 M NaCl.

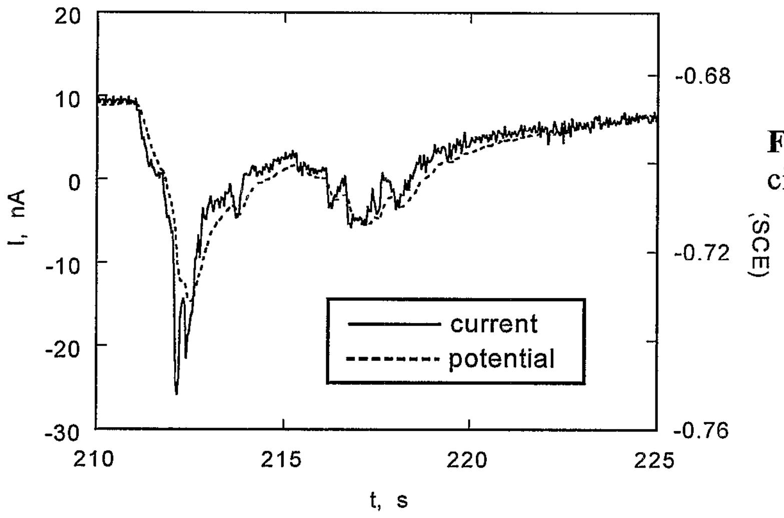

Figure 2. Details of the current and open-circuit potential shown in Figure 1.

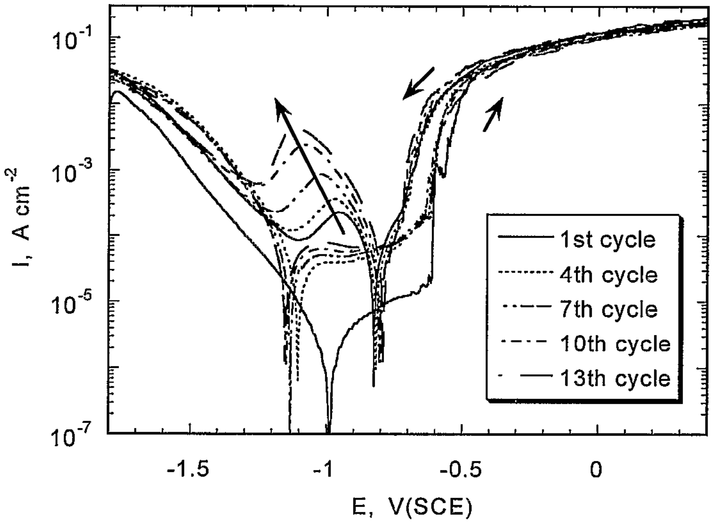

Figure 3. Repetitive polarization curves from an artificial-pit electrode between –1.8 V(SCE) and 0.4 V(SCE) in 0.05 M NaCl at a sweep rate of 4.8 mV s^{-1}.

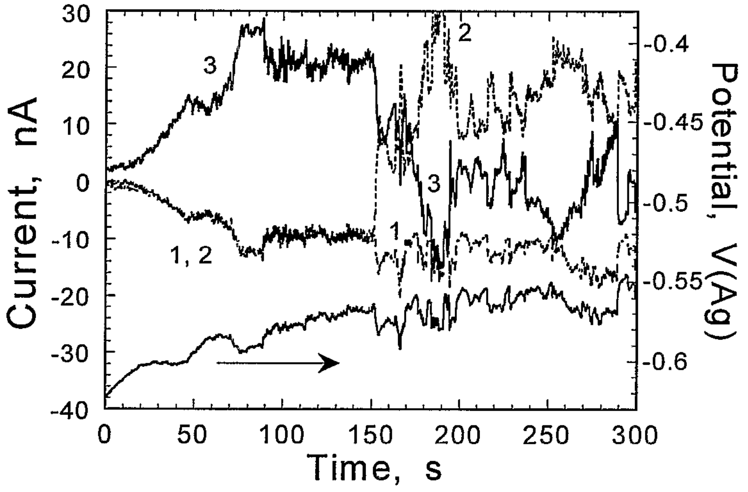

Figure 4. Current transients from three electrodes in agar gel containing 0.05 M NaCl.