

THE EFFECT OF CHROMATE CONCENTRATION ON THE  
REPASSIVATION OF CORRODING ALUMINUM

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# THE EFFECT OF CHROMATE CONCENTRATION ON THE REPASSIVATION OF CORRODING ALUMINUM

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## ABSTRACT

Current density maps of anodically polarized pure aluminum in chloride solutions were measured and the effect of chromate / dichromate buffer additions monitored. The higher the polarized potential the more chromate was required to repassivate the corroding surface. Small pits repassivated easily, crevice corrosion events were the last to repassivate. Open circuit potential measurements showed the presence of meta-stable pitting at chloride concentrations of 0.3M. The lifetime and magnitude of these metastable pits was reduced on the addition of 0.05M chromate buffer.

## INTRODUCTION

Chromate compounds are well known corrosion inhibitors for many different materials including steel [1,2,3], galvanized steel[4,5] and aluminum[2,6,7]. In recent years the power of chromate to inhibit the corrosion of aluminum in chloride containing solutions has been the focus of much research attention, because of their environmental hazard. To date, there are no widely accepted mechanisms to explain the role of chromate as a corrosion inhibitor, although several theories exist.

Chromate corrosion inhibitors are found as components of conversion coatings, paints, primers and as additives in aqueous environments. Chromate conversion coatings, formed by immersion of aluminum alloys in an acidic solution of chromate and fluoride, have an extensive history for the protection of aluminum alloys in the aerospace industry[8]. These films contain both  $\text{Cr}^{3+}$  and  $\text{Cr}^{6+}$  species, with the relative concentration being dependent upon the pretreatment procedure[9]. There is a considerable amount of interest recently in the mechanism of protection[8] offered by chromate conversion coatings and in replacement inhibitors.

In an effort to understand the role that chromate plays in inhibiting the corrosion of anodically polarized aluminum, initial experiments were conducted by Hawkins *et al*[10]. The efficient action of chromate on a corroding aluminum substrate was demonstrated by current mapping using a scanning vibrating probe and observing the corresponding current transients. The scanning vibrating probe has been used successfully to map local current densities above the surface of corroding substrates[11] and also to study the action of

corrosion inhibitors[12]. The spatial resolution of actively corroding areas has played a key role in understanding the response of a corroding surface to the addition of an inhibitor.

A recent paper by Sehgal *et al*[13] has demonstrated that a high chromate to chloride concentration ratio, in the order of 1:1 is required to affect thin film 2 dimensional pit growth. This concept is investigated here for pitting in bulk pure aluminum.

## EXPERIMENTAL

The scanning vibrating probe (SVP) used in this study was obtained from Applicable Electronics (Massachusetts). A microelectrode is mounted at the end of two piezoelectric reeds. The piezoelectric crystals are made to vibrate orthogonally by the application of two separate ac voltages having different frequencies to produce a microelectrode vibration amplitude of about 20  $\mu\text{m}$ . The variation in the electric field sensed by the microelectrode is measured with phase sensitive or lock-in detection which separates the fields in each vibration direction, because the different vibration frequencies. The current density in solution is proportional to the magnitude of the measured electric field. In this study, platinum-iridium microelectrodes, from Micro Probe, Inc. (Maryland), were used. The electrodes are coated with Parylene-C, leaving only 5  $\mu\text{m}$  of the tip exposed. To increase the surface area, platinum black is electrodeposited on the tip to a final diameter of 10-20  $\mu\text{m}$  from a solution of 1% dihydrogen hexachloroplatinate. The increased electrode area results in an increase in the interfacial impedance, improving the signal to noise ratio.

Samples of 99.999% pure aluminum were cut into 1  $\text{cm}^2$  sections and mounted metallographically using EPOFIX from Struers. The samples were abraded to 600 grit SiC, rinsed with  $18 \times 10^6$  ohm-cm Millipore water and air dried. A 3 x 3  $\text{mm}^2$  section of metal was exposed to the electrolyte by masking the remainder of the sample with Polyester 5 adhesive tape from 3M.

The SVP was vibrated in a plane normal to the surface (i.e., in a direction parallel and normal to the surface) at a height of 200  $\mu\text{m}$ . Anodic regions are represented by positive currents and cathodic regions by negative current density. The potential of the samples was controlled potentiostatically and the applied current was monitored. Throughout a silver/silver chloride (Ag/AgCl) reference electrode was used.

## RESULTS

### Applied potential of -500 mV vs Ag/AgCl

Current density mapping took 4.45 min to complete and a scan was initiated every 4.5 minutes. The entire exposed surface and areas over the tape were mapped. For each mapping scan a background current is estimated and subtracted from the measured current. Chromate inhibitor was added in the form of a pH 7 buffer solution of potassium

chromate ( $K_2CrO_4$ ) and potassium dichromate ( $K_2Cr_2O_7$ ) to avoid the effects of altering the solution pH. A typical current distribution at the start of an experiment without chromate addition is shown in Figure 1, which shows two 3-D plots of each scan. The first plot emphasizes the difference in magnitude of the current densities. The second emphasizes the location of the anodic and cathodic areas, and approximates a contour plot. In figure 1, current density is almost uniform over the exposed aluminum surface because of the proximity of many active pits. At the edges of the exposed aluminum, the current is seen to fall dramatically to background currents.

Chloride to chromate ratio of 1:2 On the addition of chromate to give a concentration of 20 mM in the 10 mM chloride solution, the current demand dramatically decreased as can be seen in the sequence of current density maps in Figure 2. After the addition of chromate buffer, the anodic currents are reduced to noise levels over the bulk of the sample. During the first scan, it is clear that the system is highly dynamic with the corrosion sites re-passivating during the scan. In the first scan, shown immediately after the addition of the chromate, the distinct high current density plateau is seen with pitting both on the plateau and on the area of low current. The remaining current density maps over the surface show a greatly reduced current at the experimental noise level, plus or minus  $50 \mu A/cm^2$  over most of the surface. A low level of activity is, however, still seen at two pits, which were initiating crevice corrosion at the edge of the sample. These pitting sites were considerably reduced in activity although not completely re-passivated.

Chloride to chromate ratio of 1:1 Crevice sites continue to grow when insufficient chromate is added to the cell as seen when 10 mM chromate is added to the 10 mM NaCl solution. The current density maps of the aluminum surface after the addition of chromate reveal the highly active crevice sites, Figure 3. The presence of chromate rapidly re-passivates pits present away from the edges of the sample, and the current at the bulk surface is rapidly reduced to background levels. However, three, then two, corrosion sites remain active at the edge of the sample. These well established pits or crevice sites remain active and continue to grow throughout the remainder of the experiment, approximately 30 minutes, with no significant decrease in anodic current measured.

#### Applied potential of -550 mV vs Ag/AgCl

Chloride to Chromate ratio of 2:1 Lowering the applied potential had as a marked effect on the ratio of chloride to chromate required to re-passivate the pure aluminum sample. The addition of only 5 mM chromate to the 10 mM chloride solution effectively re-passivates the 3x3mm aluminum sample with the exception of one crevice, Figure 4. The crevice site which did not immediately re-passivate, Figures 4(b) and 4(c), can be seen superimposed on the overall high current density of the scan just prior to the addition of chromate, 4(a). After 6 minutes in the presence of chromate the current density measured at the crevice site has been halved. Further scans of this area continued to show the presence of the active occluded site.

#### Open circuit conditions

Immersion in Chromate Buffer The open circuit potential of pure aluminum immersed in 50 mM chromate/ dichromate buffer, pH 7, was recorded at 30 second intervals, figure 5. The potential increased from -830 mV vs. Ag/AgCl to -570 mV over the course of 43 minutes. At this point a current density map of the surface was recorded. As the vibrating

probe moved over the surface at a height of 200  $\mu\text{m}$  the potential was seen to drop by almost 80 mV indicating that the aluminum surface was surprisingly sensitive to the local stirring of the solution. This sensitivity was not seen later after the onset of metastable pitting. Two additions of 50 mM NaCl solution were added to the cell 111 and 190 minutes after the start of the experiment. Decreases in the open circuit potential were seen following both additions but only on the second addition (solution concentration now 100 mM chloride in 50 mM chromate) were potential transients, caused by the onset of metastable pitting, first recorded. Further additions of chloride, to a total concentration of 300 mM resulted in a lowering of the open circuit potential to an average of  $-600$  mV with potential transients in the range of 40 to 120 mV.

Immersion in Chloride Recording the open circuit potential of a pure aluminum sample immersed in 300 mM chloride solution, Figure 7 reveals evidence of potential transients immediately after immersion. The average potential remained at about  $-740$  mV with potential transients of a magnitude up to 60 mV. Polarizing the sample to  $-400$  mV for 5 seconds did not initiate stable pitting. On the addition of 50 mM chromate/dichromate buffer, after 81 minutes total immersion time, the potential rapidly increased by 52 mV accompanied by a reduction of the measured transients to  $<5$  mV. A slow increase in average potential to  $-650$  mV is observed over the next 30 minutes. Once the open circuit potential reaches  $-635$  mV larger potential transients are initiated with amplitude in the range of 5 to 35 mV and shorter lifetime than the chloride only case, Figure 8.

## SUMMARY AND CONCLUSIONS

Polarization of the aluminum to  $-500$  mV vs. Ag/AgCl in 10 mM chloride solution produced pitting in the exposed surface area and crevice corrosion around the tape edge. The current transients monitored throughout the polarization showed a general increase in the current demand with polarization time, indicating the onset and subsequent increase in the level of corrosion activity. On adding chromate buffer to the electrolyte, at concentrations giving greater than a 1:1 chloride to chromate ratio, both the total applied current and the mapped local current densities dramatically decreased. Reduction of the concentration of the chromate/ dichromate buffer additions to a 1:1 chloride to chromate ratio did not instantly repassivate all of the pitting sites as seen by transients in the current density map. The freely exposed pitting sites are seen to repassivate preferentially in low chromate concentration, while the larger and more occluded sites adjacent to the tape showed an initial drop in current density followed by a slow reduction in current activity with time.

Lowering the polarization potential to  $-550$  mV vs. Ag/AgCl required a lower concentration of chromate to repassivate the surface than those at the higher potentials. Following the addition of 5 mM chromate buffer to the actively corroding aluminum in 10 mM chloride, repassivation of the established corrosion sites occurred quickly. The magnitude of the applied overpotential appears to dictate the repassivation characteristics of anodically polarized aluminum.

Potential transients measured at open circuit for pure aluminum in chloride solution show typical metastable pitting characteristics. The addition of small amounts of chromate to the chloride solution, Cl<sup>-</sup> to Cr<sup>6+</sup> ratio 6:1, causes the magnitude and the lifetime of the potential transient to significantly decrease.

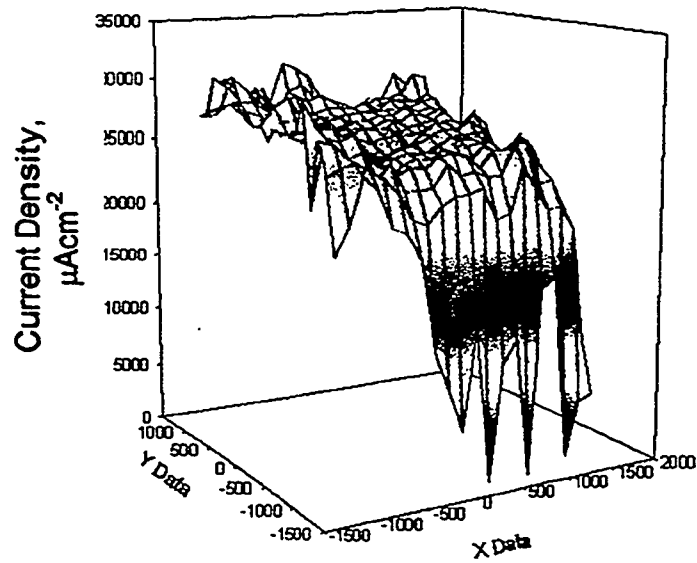
#### ACKNOWLEDGMENTS

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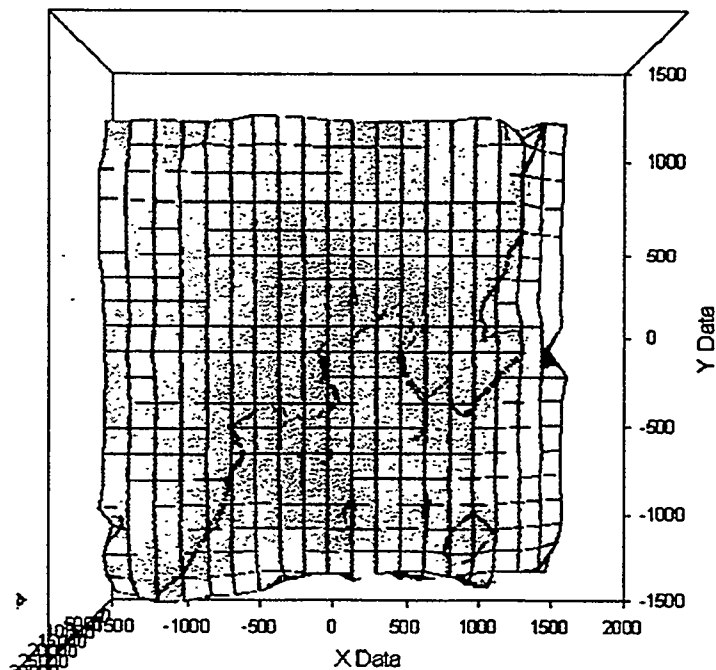
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a) 3D plot of current density over polarized aluminum surface



b) Contour plot of image in a)

Figure 1 A typical current density map for pure aluminum polarized to  $-500\text{mV}$  vs  $\text{Ag}/\text{AgCl}$  in  $10\text{ mM NaCl}$  solution.

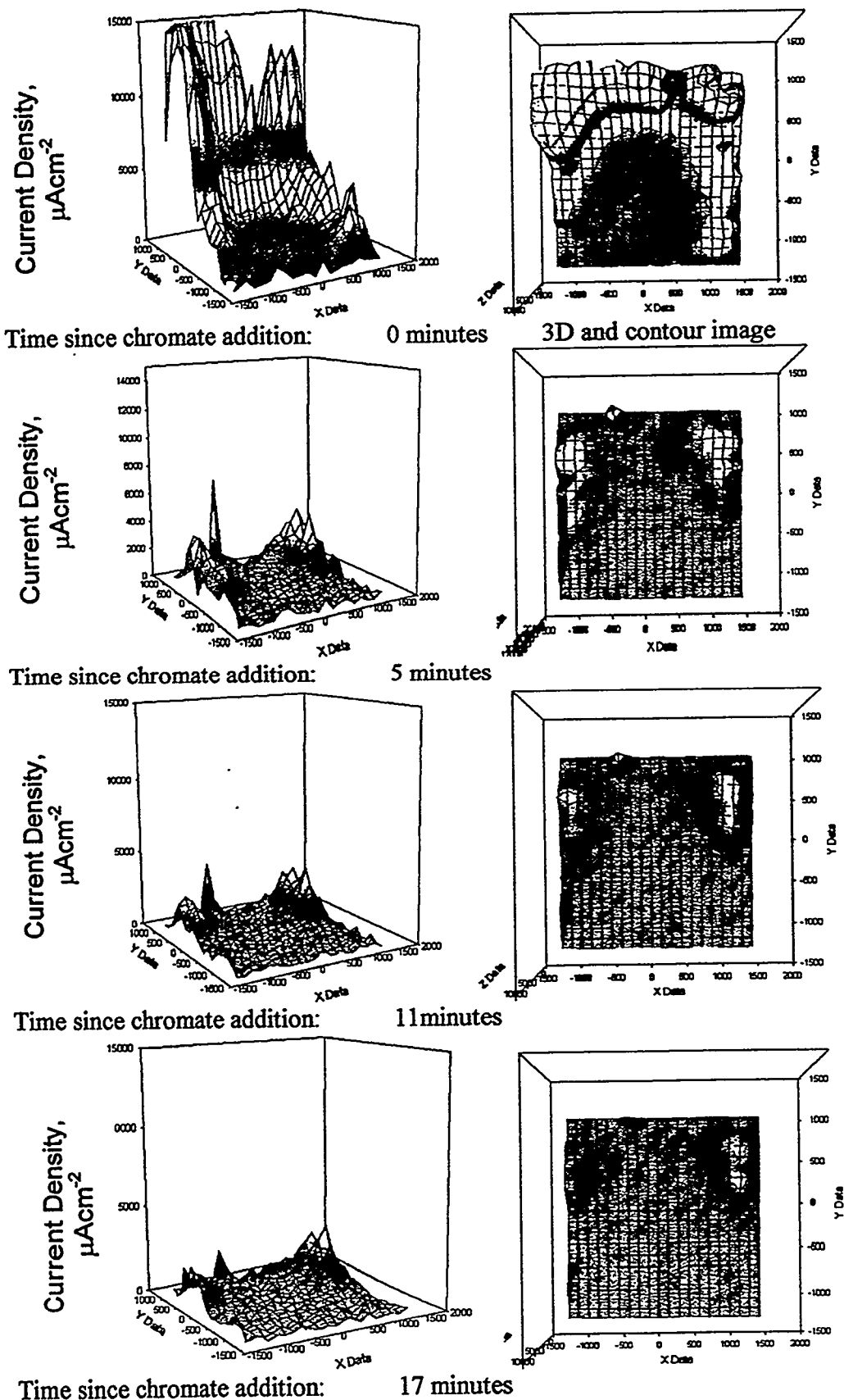
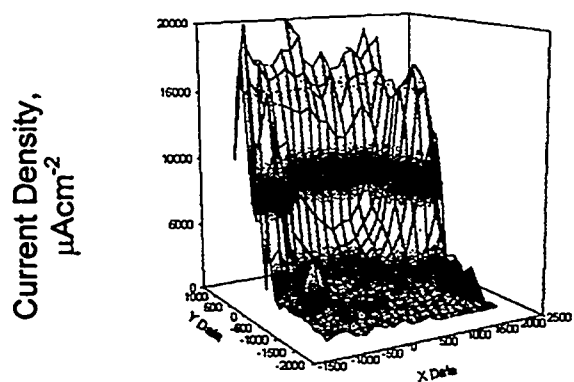
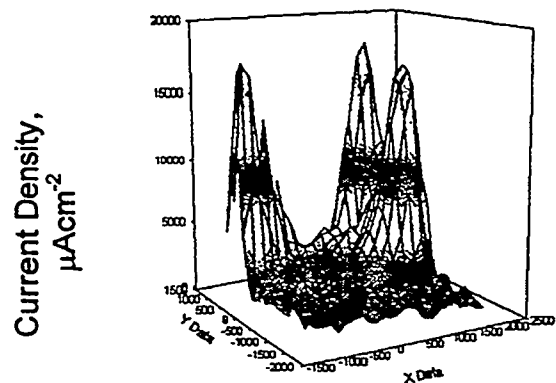
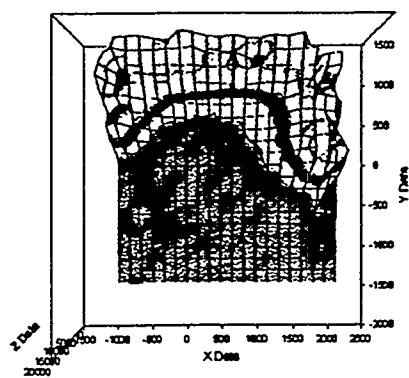


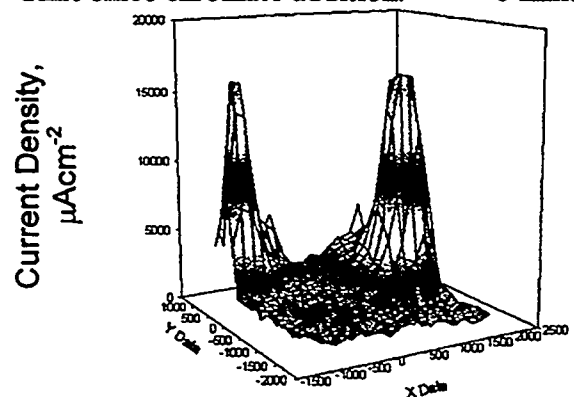
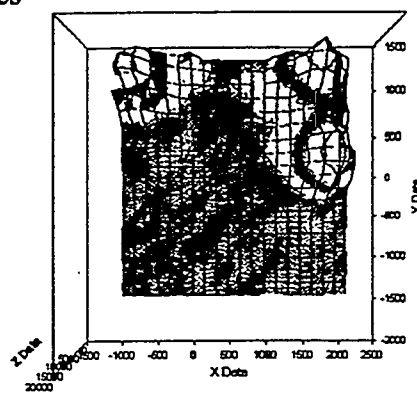
Figure 2 Current density maps after addition of 20mM chromate/dichromate buffer to 10 mM NaCl solution. Pure Aluminum sample polarized to  $-500\text{mV}$  vs Ag/AgCl.



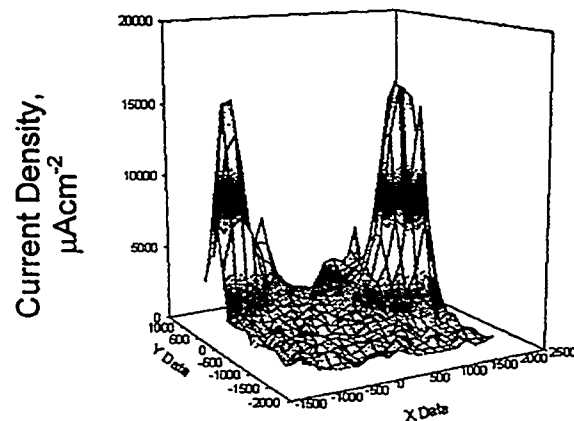
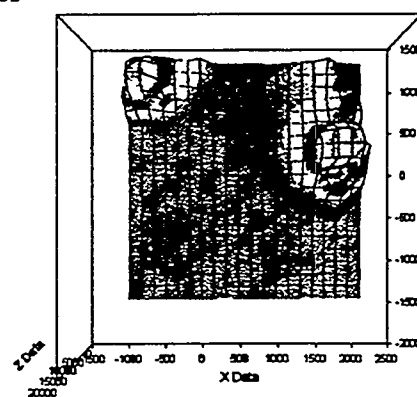
Time since chromate addition: 0 minutes



Time since chromate addition: 6 minutes



Time since chromate addition: 12 minutes



Time since chromate addition: 18 minutes

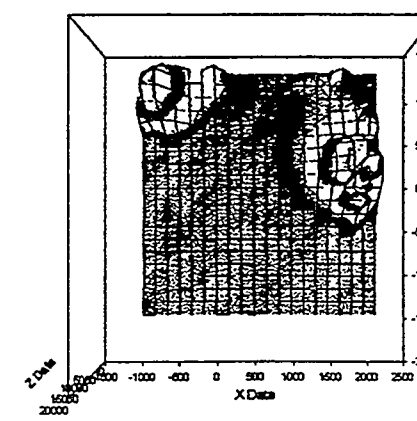
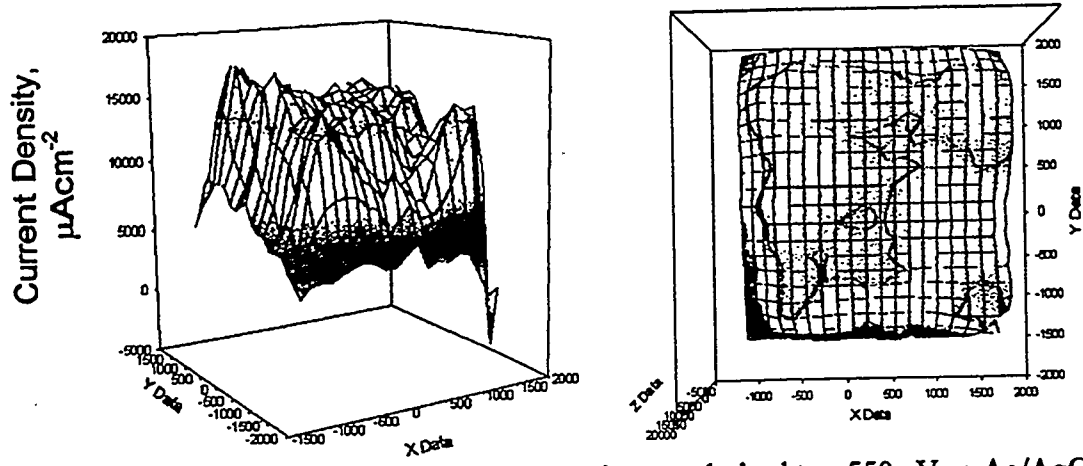
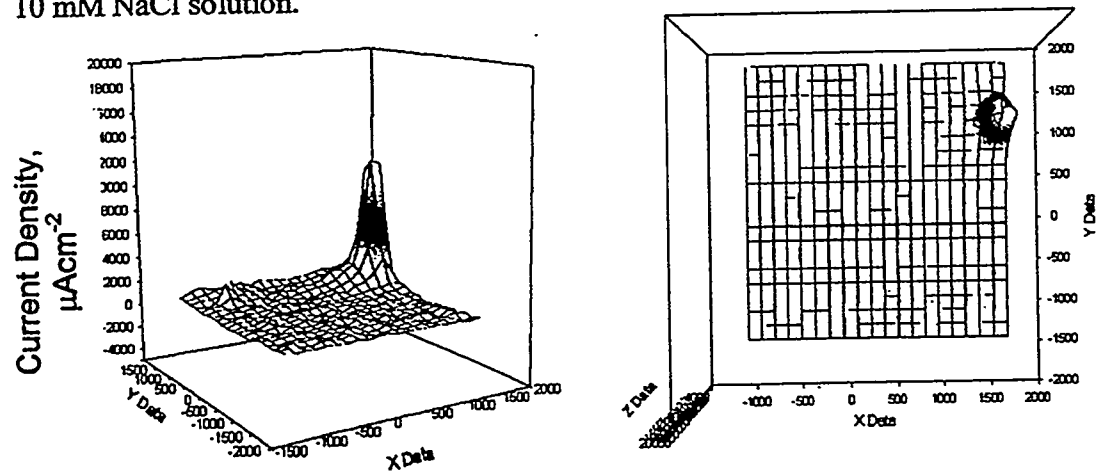


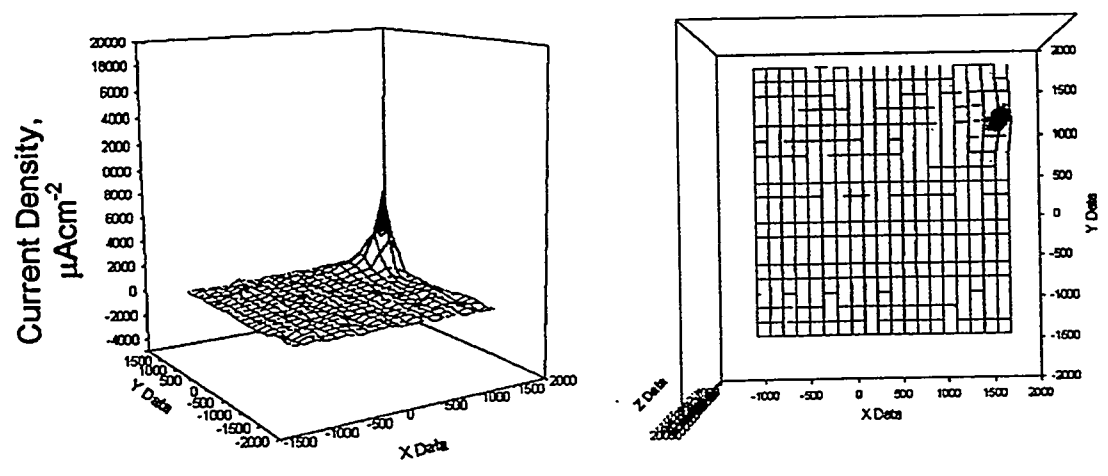
Figure 3 Current density maps after addition of 10mM chromate/dichromate buffer to 10 mM NaCl solution. Pure Aluminum sample polarized to  $-500\text{mV}$  vs Ag/AgCl



a) a typical current density map for pure aluminum polarized to  $-550\text{mV}$  vs  $\text{Ag}/\text{AgCl}$  in  $10\text{ mM NaCl}$  solution.



b) Time since chromate addition: 0 minutes



c) Time since chromate addition: 6 minutes

Figure 4 Current density maps of a) pure aluminum sample polarized to  $-550\text{mV}$  vs  $\text{Ag}/\text{AgCl}$ , b) immediately after addition of  $5\text{mM}$  chromate/dichromate buffer to  $10\text{ mM NaCl}$  solution, c) 6 minutes after chromate addition.

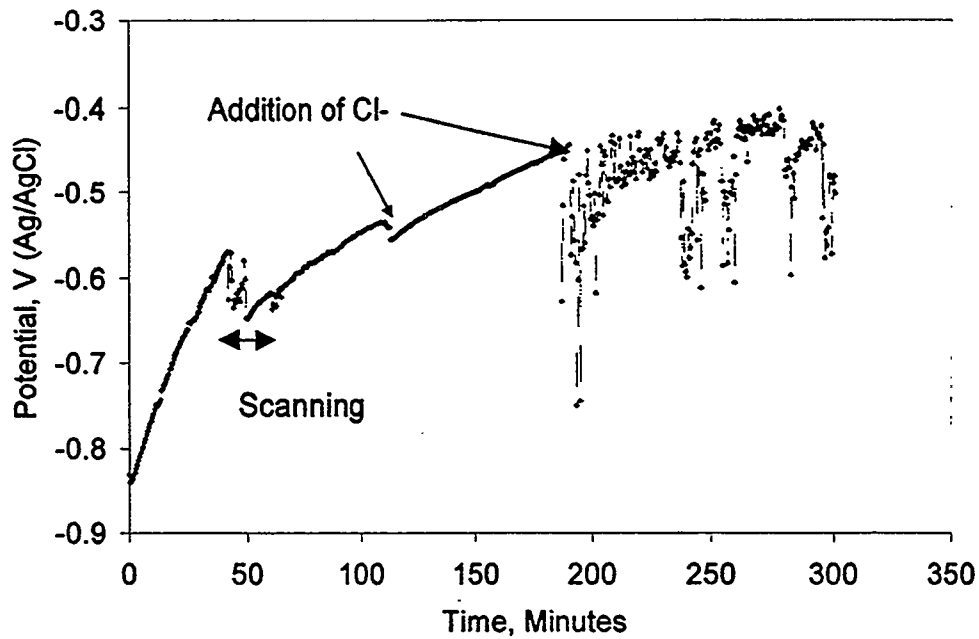


Figure 5 Open circuit potential measurements of 99.999% pure aluminum immersed in 50mM Chromate / dichromate buffer. Additions of 50mM sodium chloride solution made at the points indicated.

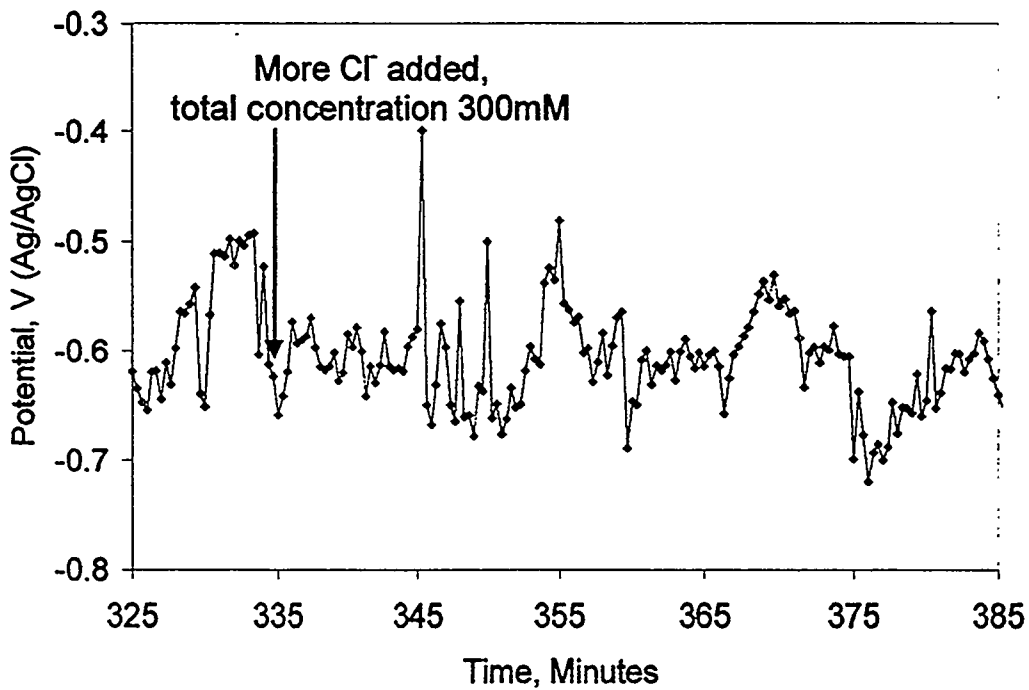


Figure 6 Open circuit potential measurements of 99.999% pure aluminum immersed in 50mM Chromate / dichromate buffer and 300mM chloride.

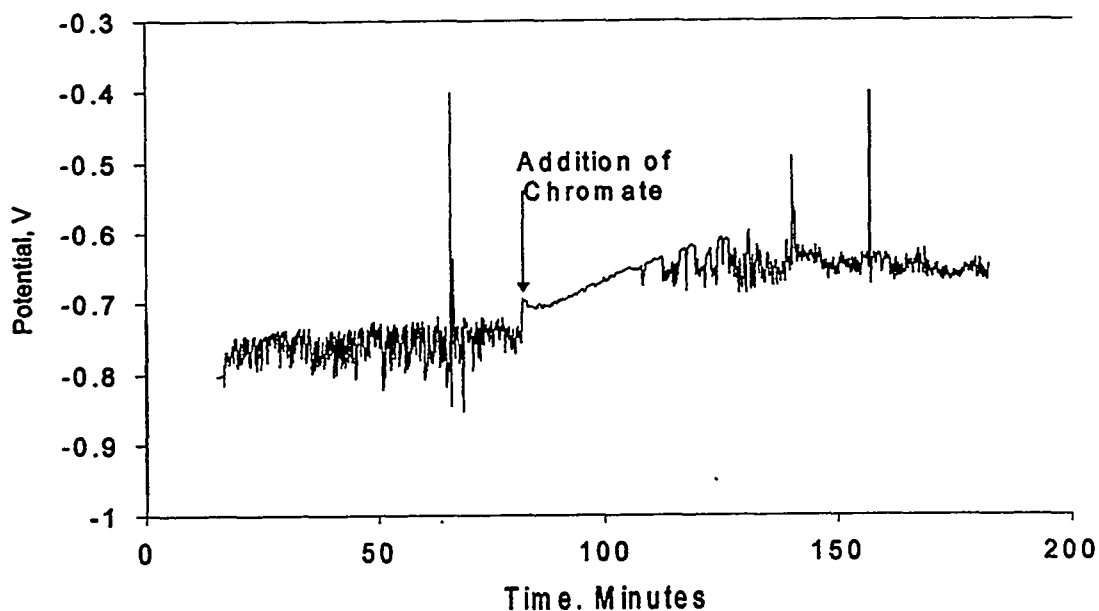
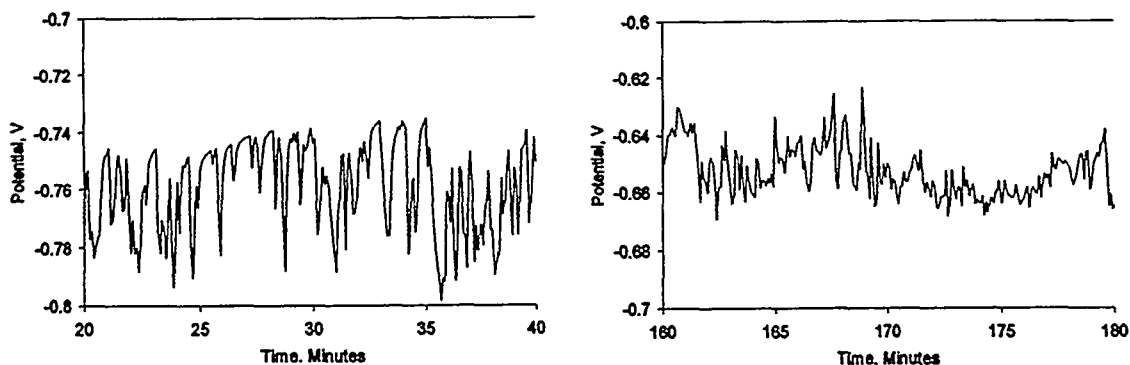


Figure 7 Open circuit potential measurements of 99.999% pure aluminum immersed in 300mM chloride solution. Additions of 50mM chromate / dichromate buffer made at the time indicated.



a)

b)

Figure 8 Potential transients measured at 5 second intervals over 20 minutes for pure aluminum in a) 300mM chloride and b) 300mM chloride with 50mM chromate