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## A Study of The Inhibition of Pitting of Aluminum by Chromate

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Chromate acts as an inhibitor of pitting corrosion of aluminum. A number of models for the inhibition have been proposed, including pH buffering effects [1], adsorption influencing other anions [2], hydrolysis of the oxide [3] and the growth of the oxide film [4], and local action theories. Local action theories have invoked processes where improved oxides form [5], precipitation and incorporation of  $\text{Cr}^{3+}$  occurs at defects [4-8] plugging mechanical flaws during crack/heal events [6-8] or precipitation-coatings develop on cathodic inclusions [6]. In order to gain more insight as to the mechanisms of inhibition a series of experiments were carried out to determine the sites of chromate interaction using both in situ and ex situ electrochemical and surface analytical methods.

The behavior of cathodic sites on aluminum was investigated by vapor depositing copper stripes to simulate more noble inclusions in the aluminum. The cathodic activity at the inclusions may be inhibited by precipitation of chromate reduction compounds and thereby reduce the pitting process. The copper stripes 0.075x3mm were spaced 1mm apart. On immersion in 1mM NaCl, the current density distribution was measured with the scanning vibrating electrode technique (SVET). SVET detects and measures the current density in solution. Fig. 1(a) shows an example of a scan over a portion of the specimen in 1 mM NaCl. Distinct cathodic current density maxima were present over most of the copper stripes but no localized anodic sites were observed. Immediately after adding chromate to give a concentration of 2 mM  $\text{K}_2\text{CrO}_4$ , the subsequent scan showed no pronounced cathodic currents over the copper, Fig. 1(b) but deposition of chromium species did take place. Secondary ion mass spectroscopy (SIMS) showed that  $\text{Cr}^+$  gave the highest yield around the periphery of the copper stripes. A broader band around this region also yielded the highest  $\text{AlO}^+$ . Some codeposition also occurred on the surface of the copper with a higher chromium concentration on the copper than the aluminum surface. These results suggest a process due either to an increased pH or co-precipitation with aluminum leads to deposition of chromium species on the cathode. This confirmed that deposition at cathodic inclusions could occur and reduce corrosion.

Activity changes at anodic sites have also been observed. A continued increase in anodic current took place after potentiostatic polarization of a 99.97% aluminum surface abraded on 600 grade silicon carbide paper and exposed at a potential of -0.55 V(sce) after a period in 10mM NaCl. The external current-time increase during polarization is shown in Fig. 2 and displayed many superimposed transients. On adding chromate to the solution after 10 minutes at -0.55 V(sce) to give 100 mM  $\text{K}_2\text{CrO}_4$ , the applied anodic current dropped to a low value. The presence of distinct current density peaks during SVET scanning were due to currents emanating from pits distribution over the aluminum surface and some pitting was observed prior to polarization as seen in Fig 3(a). On polarization marked increases in the magnitude of the currents from individual pits was seen. Both the number of active pits

and the currents from them increased with time, Fig 3(b-d). It can also be deduced that the many active sites that appeared and disappeared contributed to the external current fluctuations.

Chromate is a strong oxidizing agent but the current drop was not due to an increased cathodic activity compensating the pitting currents. This was clear from the scan started 1 minute after the chromate was added, Fig. 3(e). The previous anodic currents peaks were eliminated or reduced to levels below detection on the addition of the chromate. The inhibition of pitting was therefore due to the action of the chromate within the pits.

From these results it appears that chromate does indeed show activity at both anodic and cathodic sites during pitting corrosion. However, the processes at the cathodes although clearly detectable are secondary in the inhibition mechanisms.

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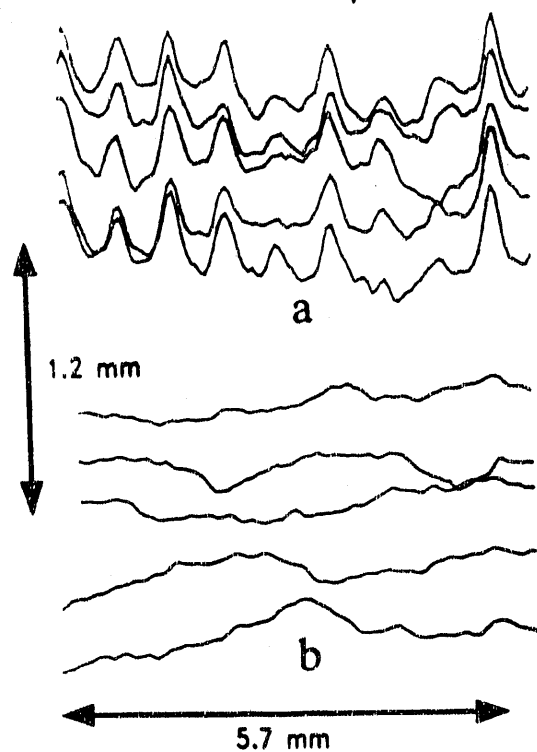
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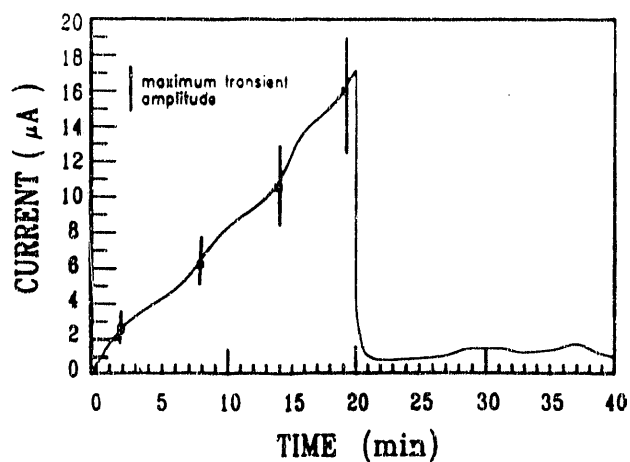
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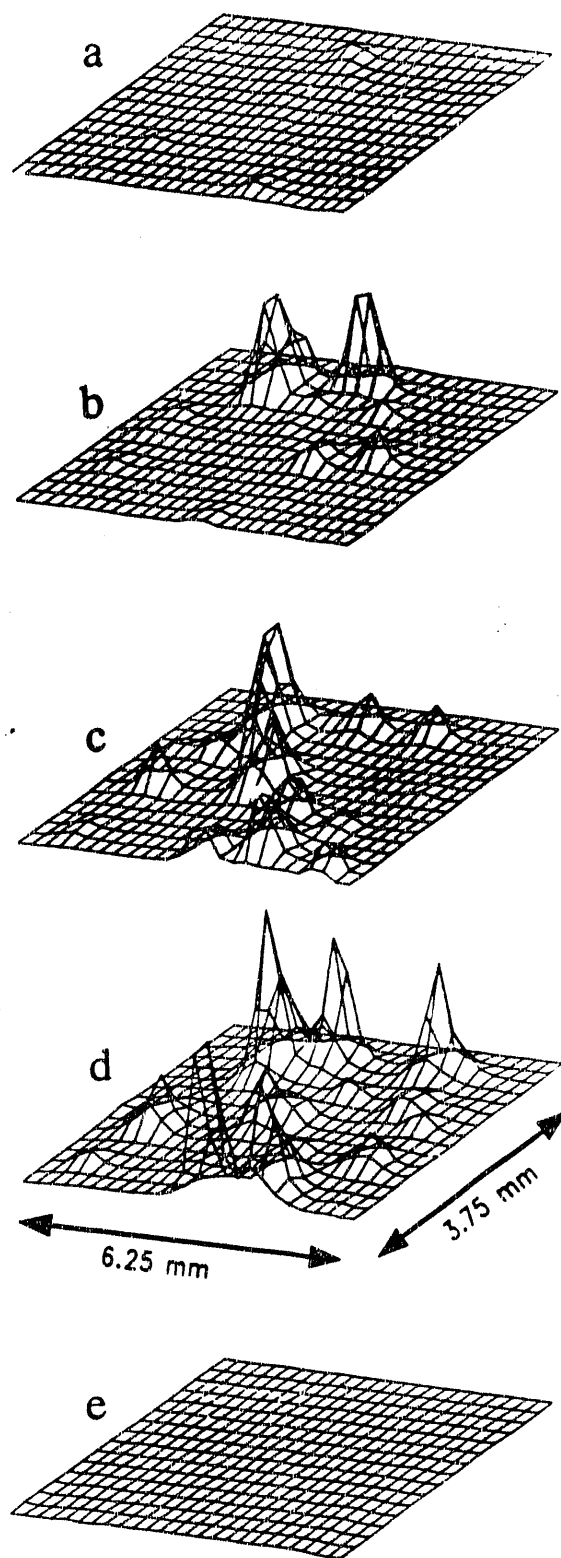
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**Figure 1.** Scanning vibrating probe measurements of current densities over an aluminum surface with copper stripes exposed to 1 mM NaCl; (a) before and (b) after the addition of 2 mM  $K_2CrO_4$  (arbitrary current density units).



**Figure 2.** Currents from abraded aluminum held at -0.55 V(sce) in 10 mM NaCl. 100 mM  $K_2CrO_4$  was added at 20 min.



**Figure 3.** SVET measurements over the sample for the test in Figure 2; (a) freely corroding, (b) after 2-5 minutes at -0.55 V(sce), (c) after 8-11 min, (d) after 14-17 min and (e) after the addition of 100 mM  $K_2CrO_4$  (similar current density units).

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