

Ionic Current Mapping Techniques and Applications to Aluminum-Copper Corrosion

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ABSTRACT

Measurements have been made of the aluminum/metal galvanic couple. A wide range of geometries were investigated varying the areas of anodic and cathodic surfaces and employing specially designed galvanic cells with crevices. In situ ionic current density mapping was used to monitor galvanic corrosion and currents flowing between separated metals was measured.

INTRODUCTION

The high corrosion rate of copper containing aluminum alloys compared to pure aluminum is attributed to both the cathodic nature of alloying element and the susceptibility of inclusions to dealloying. For example AA2024-T3 has two main precipitates found in the matrix, σ -phase $\text{Al}_2\text{Cu}(\text{Fe}, \text{Mn})$ and θ -phase Al_2CuMg . The precipitate phases have electrode potentials of -675 and -920mV vs SCE respectively (1). Trenching around σ -phase precipitates has been observed by AFM studies (2).

This present study reports an initial series of measurements that are designed to identify the important factors in the initiation and propagation of corrosion of aluminum. Metal/metal galvanic couples of various designs have been studied using very simple standard electrochemical methods and *in situ* current density mapping in solution. In principle the polarization characteristics determine the galvanic corrosion rates. However, the details of the changes in the polarization characteristics complicates a quantitative prediction of the corrosion rates. The polarization behavior changes with time and concentration buildup in pits and crevices as they are formed, as well as at the freely exposed anode and cathode. The extent of the chemical changes are future complicated by the close proximity of anodes and cathodes as is the case with most corroding systems. In order to start to try and take the latter effects into account current density mapping has been used as it closely represents many of the corrosion processes.

Ionic current density mapping has been used to investigate different types of corrosion(3); crevice(3); pitting(4); and intergranular corrosion(5). The technique, utilizing a scanning vibrating microprobe, detects currents flowing in solution. The vibrations transform a dc potential gradient due to current flow in a resistive solution. The vibration is used to convert the dc gradient to an ac signal allowing cleaner signal amplification. With galvanic corrosion the cathodic areas are well defined but it is necessary to spatially resolve anodic sites which can develop adjacent to the cathodes or on the exposed aluminum surface.

EXPERIMENTAL

The Applicable Electronics (Forestdale MA) current density mapping has been in detail in another publication (6). Simply a fine tipped Pt/Ir probe with a 20 μm diameter of Pt black is scanned in a plane parallel to and 100-200 above a sample. The probe vibrates in the X and Z directions at different frequencies with amplitudes. Phase sensitive detection is used to measure the variation in the electric field in each vibration direction. The current density is proportional to the magnitude of the measured field and can be calibrated using a point source. All samples were masked off with 3M type 5 tape, leaving and exposed surface area of approximately 3 x 3 mm. In addition a visual record is kept of the samples during the experiment to correlate appearance changes with anodic currents and to assist in distinguishing between pitting and crevice corrosion. In addition a visual record is kept of the samples during the experiment to correlate appearance changes with anodic currents and to assist in distinguishing between pitting and crevice corrosion.

Couples of noble metals imbedded in Al were tested. Cu and Pt wires were placed in axial holes in rods of pure 99.999% and then swaged to contact the wires and Al. The resulting wire diameter was 0.5 mm. Using a similar approach a copper wire in a Teflon shrink tube was imbedded in Al and electrical contact was made externally. The area exposed to solution was limited with adhesive tape (3M Type 5) with a 3x3 mm cut out window.

Samples of Al thin films with copper disks have been described previously (7). Al films, 150-200 nm thick were deposited by on a Si (100) substrates. The samples were then exposed to air to form a native oxide. Photoresist was spun onto the samples and was defined using photolithography. Copper was then electron-beam evaporated through the openings in the photo resist. The photo resist layer was removed with acetone.

Couples of 1 cm^2 abraded 99.99 % Al foil and a 3 mm diameter Cu rod were also tested. The immersed end of the Cu rod was coated except for 3mm. A 3 mm plastic rod was also used schematically shown in Fig. 1 When only the Cu rod was used its cross section was pressed against the Al to form a crevice. When the plastic rod was pressed against the Al foil the Cu rod was immersed in the solution and electrical connected externally to the Al through a 1000 Ω resistor, which allowed for measurements of the current

Reagents used were of analytical or laboratory grade. All solutions used were made with 18M Ω de-ionized water.

RESULTS AND DISCUSSION

Current Density Mapping

Pt-Al Couples

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A 3 x 3 mm area, of pure Al and galvanically coupled embedded Pt wire, was mapped in 50 mM NaCl. Pt, as seen in Fig. 2, acts as a very effective cathode and strong currents were detected on immersion, which grew to a maximum after 20 minutes immersion and then decreased. Several anodic sites formed quickly. Most were located on the exposed surface. Pits on the freely exposed surface were evident as seen from the buildup of corrosion products in video images after 30 min, which continued to darken with time. The anodic sites, as determined from the current maps were transitory, but the sites on the freely exposed surface all showed buildup of corrosion products indicating that they that remained active with varying intensity throughout the measurement. The site towards the bottom right of the current density maps in Fig. 2 was formed at the corner of the tape and was probably stabilized by a crevice. A second "stable" site directly above the Pt seen after 40 min, also remained active but showed very low currents after 100 min, was also very close to the tape. A third site that showed a high degree of stability especially after 100 minutes, had deposited products away from the tape and did not appear as a crevice corrosion site.

In a number of experiments over prolonged exposure time of 60 min, a cathodic tail was observed extending from the Pt disk. The extended cathodic region appeared over the direction of the abrasive lines. The cause was associated with the surface preparation by abrasion. Pt particles from the wire were carried and deposited onto the Al where they behaved as cathodic sites. It was interesting that the tail was only observed after a rather long period of time as they must have been active throughout the measurement.

Couples of Deposited Cu-Al Films

On immersion in 50 mM NaCl the initial current density map, Fig. 3., showed high currents. The five cathodic locations over the deposited Cu disks were clearly seen with one very active anodic site in the lower right hand corner. The location of this anodic site was at the edge of the tape used to mask off the sample. The site either initiated in a crevice or rapidly turned into crevice corrosion. The anodic site remained active throughout the experiment and the path of the dissolution under the tape appeared random. As time progressed the cathodic sites changed in character and the currents from the anodic site concomitantly decreased. After 20 minutes of immersion there was a significant decrease in the cathodic currents over the five Cu sites. No anodic currents were measured around the Cu discs and once again the intense cathodic currents masked any weaker adjacent anodic current however as a visible gap formed around the edge of the Cu disk. Undermining of the Cu was observed optically as the currents from the Cu decreased. The observations confirm other studies of similar samples that demonstrated Al dissolution under the Cu (7). After 100 minutes only 4 Cu sites remained active. The current flow from the Cu disk closest to the anodic site was the first to disappear and after 160 minutes only one Cu site remained active. Each Cu disk probably became inactive once the physical connection with the Al matrix had been lost (7). As the Cu became isolated from the Al thin film, the Cu was then able to dissolve. At the end of the experiment all the Cu discs had dissolved from the sample. EDX analysis was unable to locate any Cu in the sample.

Cu-Al Couples with a Crevice

Under many conditions the Cu and Al are in direct contact and the Al corrodes in the crevice between them. Using an apparatus similar to that in Fig. 1, except the Cu rod replaced the plastic rod shown, it was found that crevice corrosion did take place between the Cu and the Al. With the apparatus shown in Fig. 1 and the plastic rod pressed against the Al, crevice corrosion again took place where the plastic was in contact with the Al in a 0.1 M NaCl solution. When no connection was made to the Cu no crevice corrosion was observed under the plastic after similar times of exposure. The current and potential variations were measured during the exposure and are shown in Fig. 4 and 5 plotted respectively as a function of time and against each other. After contacting the metals the current decreased with time. Smaller potential changes were observed as the potential first decreased and then showed a small increase. A plot of the current and potential in Fig. 4 shows the locus decreasing to a minimum and then increasing. The observed changes were dominated by a decrease in current due to polarization of the Cu. This is illustrated by the schematic polarization curves superimposed on the current-voltage curve in Fig. 5. The arrows indicate the polarization changes for anode and cathode. A greater degree of polarization is noted for the cathode indicating changes at the copper electrode dominated the decrease in the current whereas the potential of the Al accommodated the current changes with little effect on its potential.

CONCLUSIONS

The galvanic corrosion of Al in contact with Cu appears to be dominated by crevice corrosion probably initiated by pitting. For Pt with its greater current intensity, pits appear to be more stable and continue to decorate the Al surface even though the currents were below detection with the vibrating probe

Crevice corrosion was not dependent on the proximity of the Cu cathode as similar crevice corrosion processes took place under Cu and plastic. The cathode is polarized to a greater extent than the anode.

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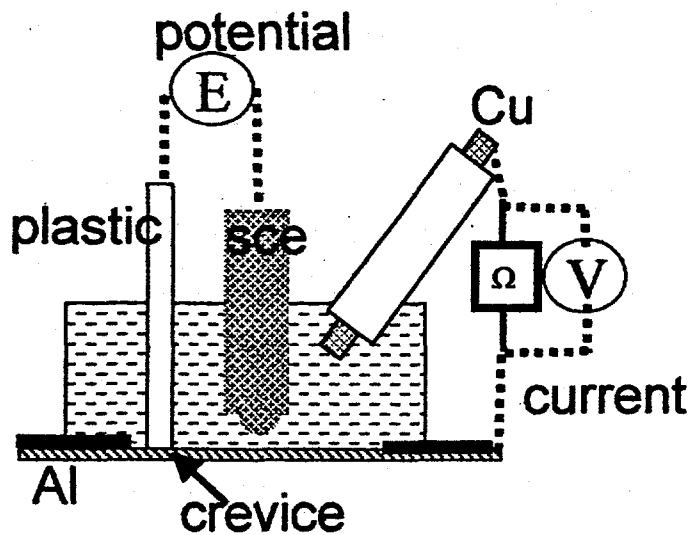


Figure 1 Schematic of apparatus for studying the effect of a crevice during crevice corrosion

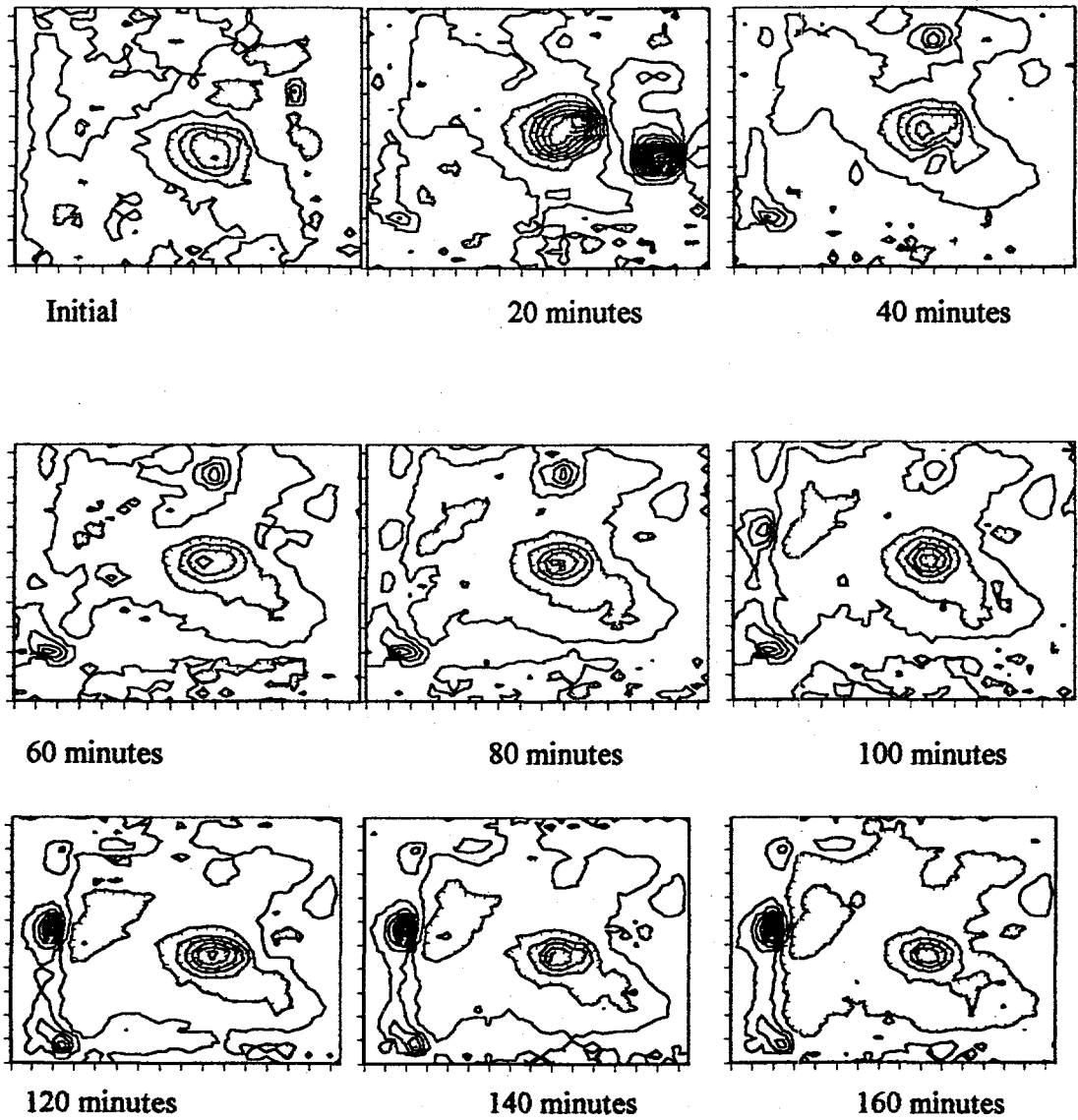


Figure 2 Pt wire inside a pure Al sample. High cathodic currents are measured centrally located over the Pt and several active anodic sites are detected around the edge of the exposed Al sample.

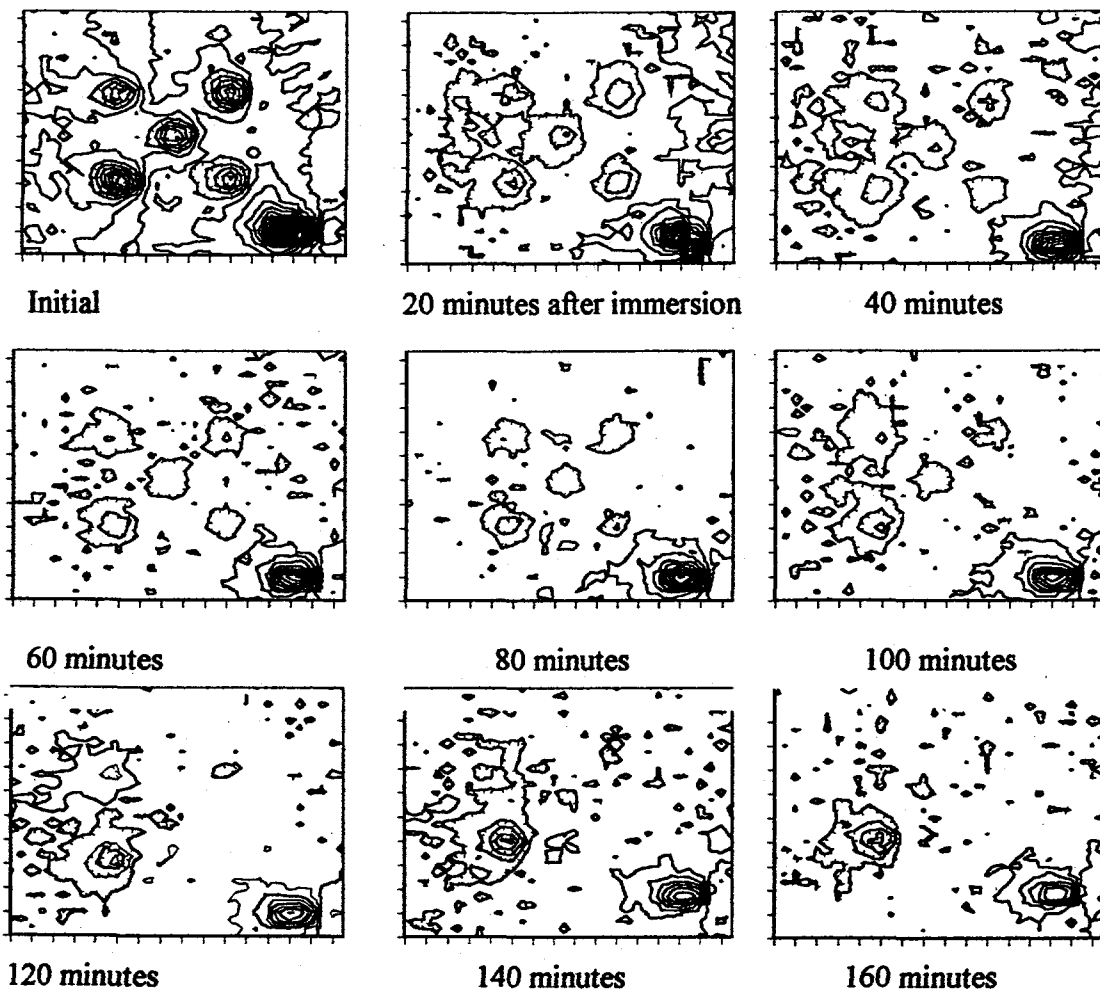


Figure 3 Current density maps over 5 Cu discs evaporated onto a thin film of Al. A sample area of 3 x 3 mm was exposed to 50 mM NaCl.

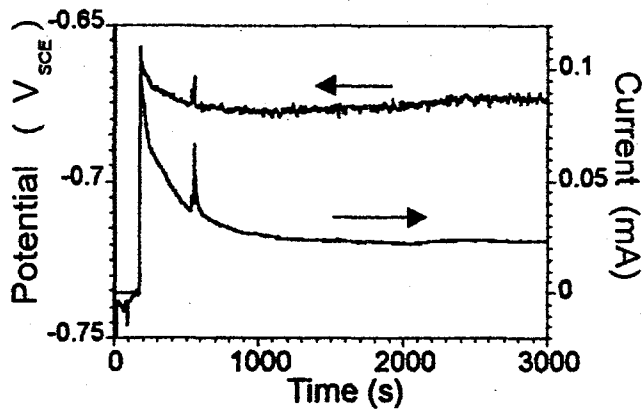


Figure 4 Variations of the potential of Al and the current flowing between an Al /Cu couple with a crevice formed between the Al and a plastic rod.

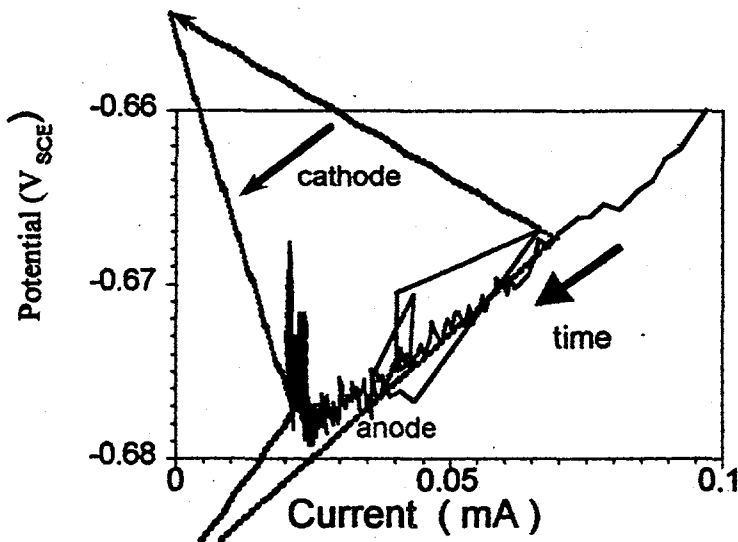


Figure 5 A plot of the current and potential shown in Fig. 4 for an Al/Cu couple. Superimposed on the curve is an Evans type diagram showing anodic and cathodic polarization lines that demonstrate a greater increase in cathodic polarization leading to the observed changes rather than a decrease in anodic polarization.