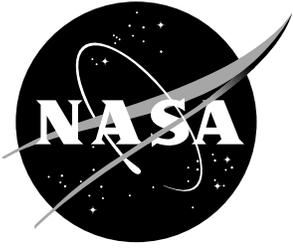


Study of Localized Corrosion in Aluminum Alloys by the Scanning Reference Electrode Technique

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TECHNICAL PAPER

STUDY OF LOCALIZED CORROSION IN ALUMINUM ALLOYS BY THE SCANNING REFERENCE ELECTRODE TECHNIQUE

INTRODUCTION

Corrosion of aluminum alloys is generally measured on a macroscopic scale using a relatively large surface area of a test specimen and measuring the corrosion currents. However, the corrosion is generally not uniform on a microscopic scale, as evidenced by pitting in many cases. Recent work with aluminum-lithium (Al-Li) alloys indicates that they are susceptible to pitting corrosion,¹ a localized corrosion phenomenon. Recently a technique has been developed that allows the measurement of localized corrosion and is called the scanning reference electrode technique (SRET). This report describes this new technique and compares the results with those obtained with general corrosion experiments. Wrought 2195 (Al-4.0Cu-1.0Li) alloy, 2195 alloy welded with 4043 filler material (Al-5.2Si), and wrought 2219 (Al-6.0Cu)-T87 alloy were used in this study.

THE SRET

The SRET instrument shown in figure 1 is commercially available from EG&G Princeton Applied Research Corp. (EG&G-PARC). It has the capability to measure microgalvanic potentials close to the surface of materials, and it allows in situ examination and quantification, on a microscopic scale, of electrochemical activity as it occurs. The SRET is microprocessor controlled, and electrical potentials are measured by a special probe capable of translation in the X- and Y-directions. The specimen in the form of a cylinder is held in a vertical position and rotated around the Y-axis. The scan is synchronized with a display monitor and the resultant data are shown in the form of line scans or two-dimensional area maps. The width of the area maps (X-direction) can be set at will using the zoom-in feature of the experimental setup. The height of the area maps (Y-direction) is set automatically by the control software according to the proper aspect ratio. Movement of the scanning probe during data collection is in the Y-direction. Direct measurement of surface potentials, showing anodic and cathodic areas, at discrete positions on the sample surface may be taken and stored for time-related studies. Because the minimum detectable signal is on the order of 1 mA/cm^2 , a potential must be applied to the sample to increase the corrosion current to at least this level. This is accomplished by means of a separate potentiostat coupled to the SRET system.

EXPERIMENTAL PROCEDURE

Corrosion specimens consisted of cylindrical metal rods 10.2-cm (4-in) long. The rod diameter was 1.27 cm (0.5 in) for the 2219-T87 alloy and 1.21 cm (0.476 in) for the 2195 Al-Li alloy. In the case of welded 2195 Al-Li alloy, the final rod diameter was 1.12 cm (0.44 in). These rods were first turned to a diameter of 1.21 cm (0.476 in), after which a longitudinal V-groove, 0.318-cm (0.125-in) deep, was machined along the entire length of the rod. The V-groove was then filled using 4043 filler by tungsten

inert gas welding and subsequently machined down to a smooth circular surface with the 1.12-cm (0.44-in) diameter.

For each experiment, the test specimen was mounted in the collet of the SRET, and the probe, counter electrode, and reference electrode were also placed in their positions in the machine. The entire assembly was immersed in a corrosive medium consisting of a 3.5-percent sodium-chloride (Na-Cl) solution. About a 5.1-cm (2-in) length of the metal sample rod was thus exposed to the corrosive medium. A potential of -0.70 V with respect to the saturated calomel electrode was then applied to the sample by a computer-controlled EG&G model 273A potentiostat. During data collection, the sample was rotated at 100 revolutions per minute (r/min). Map scans were taken beginning and ending at equal distances from the zero point of the SRET, such that a distance of 3.0 cm of the sample circumference was displayed on the map (X-direction). In the case of the welded 2195 Al-Li alloy sample, the weld was positioned 180° from the zero point of the SRET so that the welded area appeared in the middle of the map scan. The experiments were set up in such a way that all maps had a width of 3.0 cm (X-direction) and a height of 2.25 cm (Y-direction). Movement of the probe during the scan is in the Y-direction.

A total of six area maps were collected for each sample, requiring about 3.5 h to complete. After completion of each map scan, the data were stored in a separate file for later display and measurement. Approximately 18 min were required for the completion of each map scan. A 10-min delay was then imposed before the start of the next map scan, so that there was a total delay of 28 min between each of the scans.

As mentioned previously, a potential of -0.70 V (SCE) was supplied to each sample by the potentiostat. For the 2219-T87 Al alloy and the 2195 Al-Li alloy, this potential was approximately 100 mV above the corrosion potential E_{corr} (-0.80 V). For the welded 2195 Al-Li alloy, E_{corr} was higher at about -0.756 V. As a result, the difference between the applied potential and E_{corr} was lower, only 56 mV above the corrosion potential. Currents increased gradually during data collection as corrosion progressed. Currents for the 2219-T87 Al alloy and the 2195 Al-Li alloy were similar, but that for the welded sample was lower because of the reduced difference between the applied potential and E_{corr} .

After data collection was completed, each map was displayed on the computer screen and the proper palette for display of the map features was selected. Measurements of the topography of the various map features (potentials for anodic and cathodic regions) were obtained using software developed by EG&G-PARC for this purpose.

RESULTS AND DISCUSSION

Localized Corrosion in 2219-T87 Al Alloy

Potential maps for the 2219-T87 Al alloy, obtained by the SRET, are shown in figures 2 and 3. The map in figure 2 was obtained after 2 h with the sample at a potential of -0.70 V, while the map in figure 3 was obtained after 3 h at the same potential. The current after 2 h was 2.90 mA/cm² and after 3 h was 3.01 mA/cm². Measurements of the surface potentials for various features are recorded within each map. Positive features are cathodic, while negative features are anodic.

As seen from the map of figure 2, anodic and cathodic regions are rather broad, and there are not a great many features interspersed in these regions. The map in figure 3, obtained 1 h later (3 h), does

not show significant change except for the generally anodic region just to the left of the map center. Here, the anodic and cathodic areas seem to be passivating somewhat locally, the cathodic areas becoming less positive and the anodic areas less negative. This situation is normal, but generally not true for the sample as a whole, where there is no significant change from figure 2 (2 h) to figure 3 (3 h).

Localized Corrosion in 2195 Al-Li Alloy

Potential maps for the 2195 Al-Li alloy are shown in figures 4 and 5. The map in figure 4 was obtained with the sample at a potential of -0.70 V after 2 h. The current at this time was 2.63 mA/cm². The map in figure 5 was obtained after 3 h with the sample at the same potential. The current at this time was 3.07 mA/cm². As the maps show, there are many more features in the 2195 Al-Li alloy than were present in the 2219-T87 alloy, although, generally, anodic and cathodic regions are rather broad and occur in alternating sequence. There is, however, a greater variation in the potentials of features within these regions, although they are of the same sign. Some of the cathodic areas are more positive than was the case in 2219-T87 Al alloy, and many of the anodic areas are much more negative. This result indicates a greater tendency toward pitting for the 2195 Al-Li alloy.

Localized Corrosion in Welded 2195 Al-Li Alloy

Potential maps for the welded 2195-T87 alloy are shown in figures 6 and 7. Again, the map in figure 6 was obtained after 2 h with the sample at a potential of -0.70 V. The current at this time was 1.44 mA/cm². The current after 3 h at the same potential was 1.49 mA/cm² (fig. 7). Because the currents were much lower than those for the first two cases (the potential applied to the sample was only 56 mV above E_{corr}), these maps, especially that at 2 h, are somewhat affected by noise. This situation improved with time. As the figures show, the potential map for the welded material is quite different from those for the wrought materials, the structure being quite striated in the direction of the weld (Y-direction). The width of the weld, as measured on the sample surface, was 0.75 cm after the welded sample rod was reduced from a diameter of 1.21 cm (0.476 in) to a final diameter of 1.12 cm (0.44 in). As seen from figures 6 and 7, the entire welded area is cathodic. Its width, as obtained from the map, is 0.95 cm. This is slightly larger than the weld width measured on the sample (0.75 cm). The strongly anodic regions bordering the weld bead, therefore, probably lie in the heat affected zone (HAZ) of the welded sample rod. There is not a great deal of structure change between the maps taken at 2 and 3 h. The depth of the anodic features at the weld edge indicates a tendency toward pit formation in the HAZ.

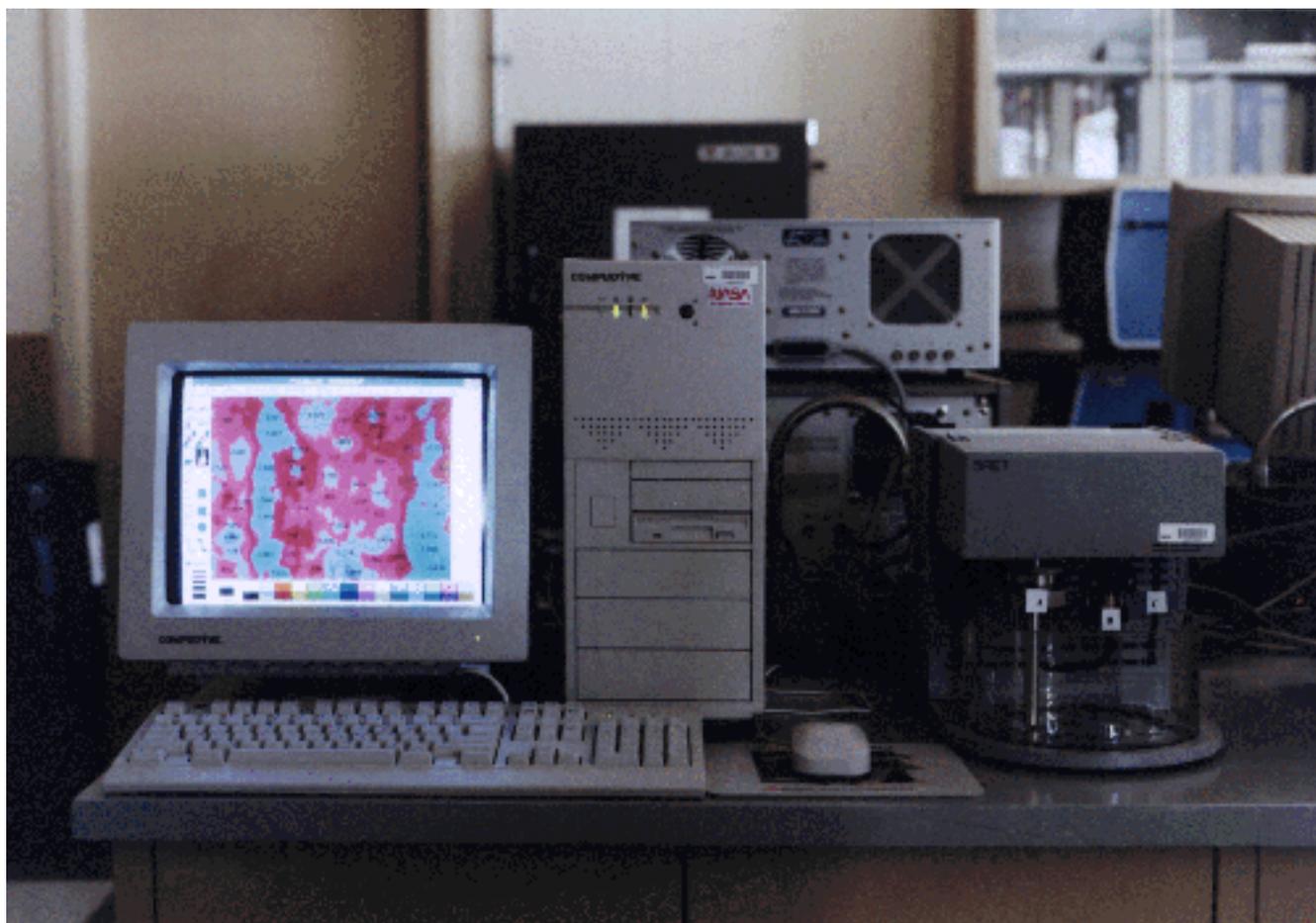
Comparison With General Corrosion Results

Curves taken from previous work,¹ showing the variation of corrosion currents with time for 2219-T87 and 2195 alloys, are shown in figure 8. These results were obtained using the dc polarization resistance (PR) technique and represent the overall corrosion behavior for these materials without any applied potential. The solid and dotted lines are the result of linear regression fits to the observed data and show that the overall corrosion currents, and hence corrosion rates, decrease with time. Average corrosion currents over a 21-day period were 0.221 $\mu\text{A}/\text{cm}^2$ and 0.250 $\mu\text{A}/\text{cm}^2$ for the 2219-T87 alloy and the 2195 alloy, respectively. The linear regression fits to the observed data are very close for the entire period of measurement, and show that the overall corrosion rates are about the same for both alloys. More scatter in the data is present for the 2195 Al-Li alloy, which is usually an indication of a greater tendency toward pitting. These results are consistent with the results obtained with the SRET.

SUMMARY

Although measurements of the general overall corrosion rates for 2219-T87 Al alloy and 2195 Al-Li alloy show little difference, measurements of localized corrosion in these materials, made possible by the SRET, show marked differences in the pattern and strength of anodic and cathodic corrosion sites. The 2195 Al-Li alloy shows far more structure in this regard than does 2219-T87 Al alloy. Further, these sites show in general a greater negativity for the anodic sites, which indicates that the 2195 Al-Li alloy is more prone to pitting.

The most interesting result was in the case of the welded 2195 Al-Li alloy, welded with 4043 filler. The weld bead was entirely cathodic, with all neighboring features aligned parallel to the weld. Further, the regions on either side and bordering the weld, lying mostly in the HAZ, were strongly anodic. An electrochemical cell, therefore, exists between the weld and the HAZ. The highly negative potentials of the anodic regions can be taken as an indication that corrosion in the welded material readily occurs at the weld edges, with a strong tendency toward pitting in the HAZ.



(A–metal sample; B–probe; C–counter electrode)

Figure 1. The scanning reference electrode system.

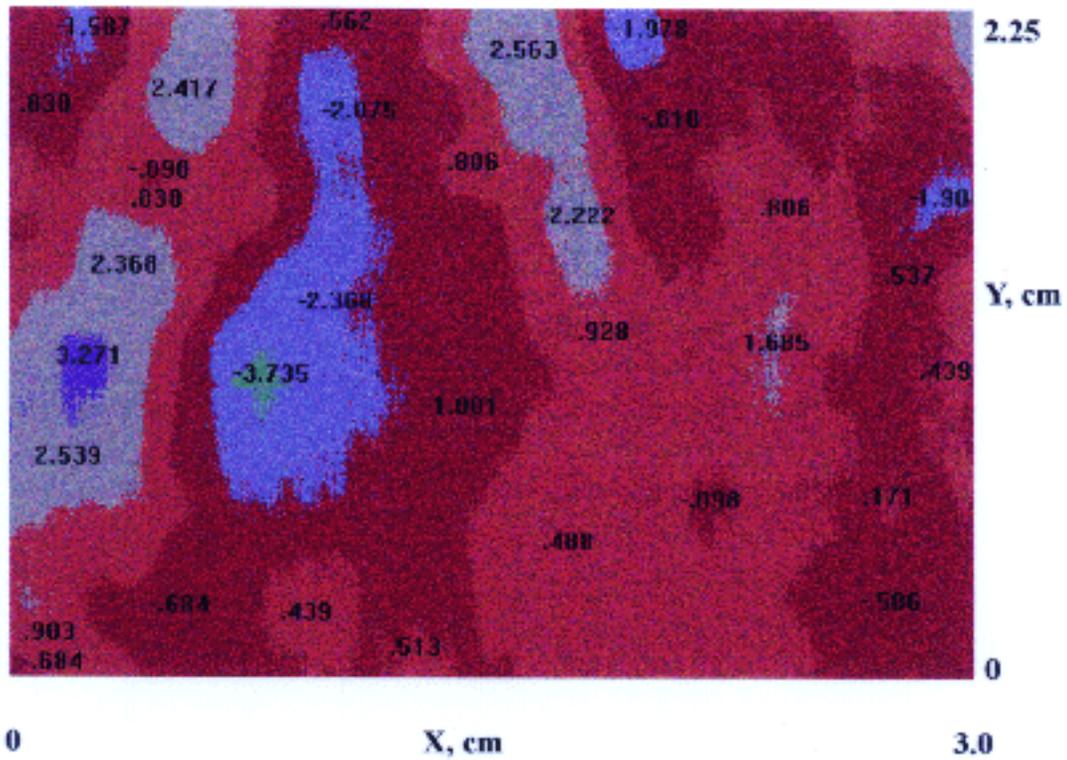


Figure 2. Localized Corrosion in 2219-T87 Al Alloy After 2 Hours

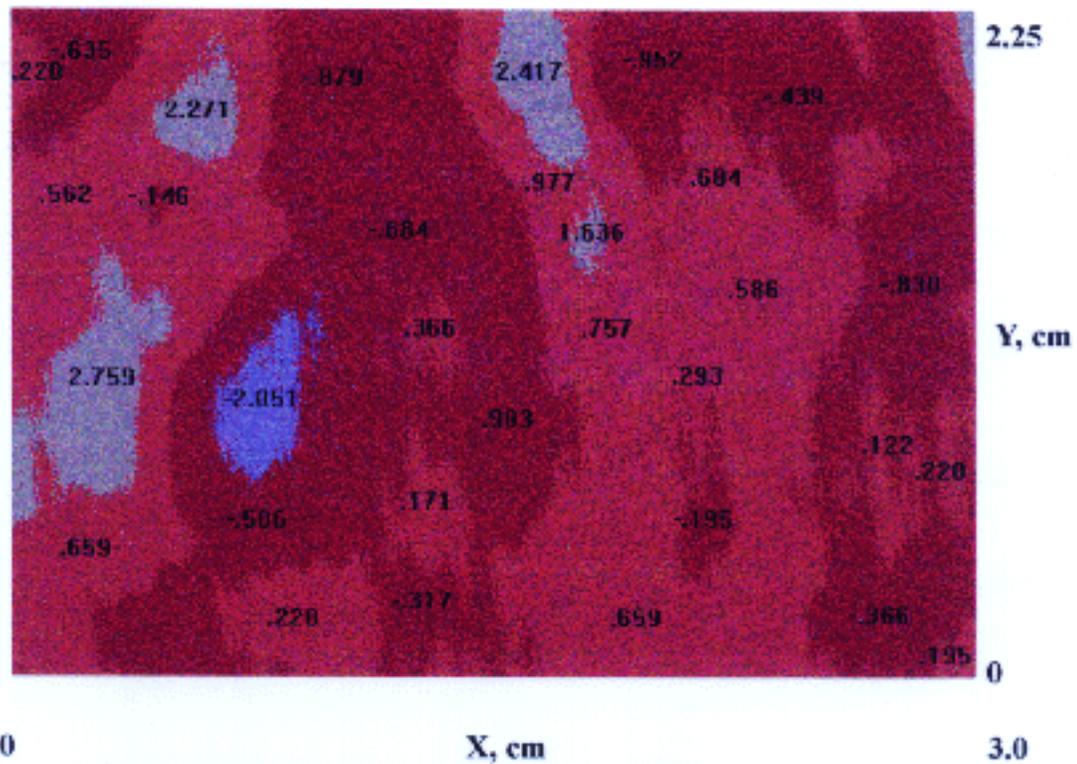


Figure 3. Localized Corrosion in 2219-T87 Al Alloy After 3 Hours

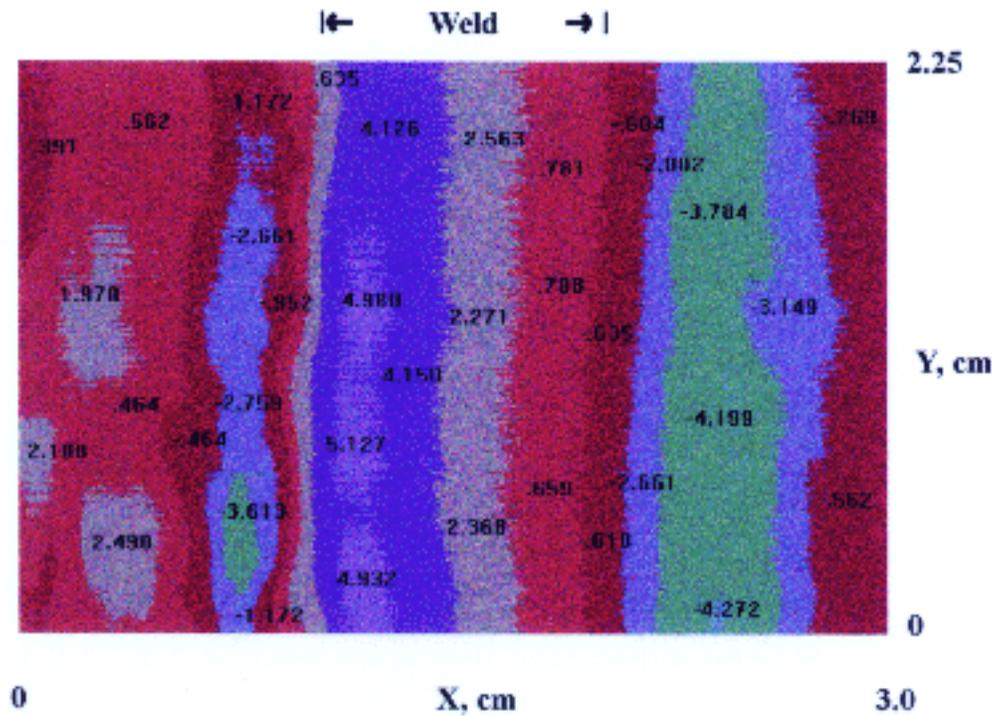


Figure 6. Localized Corrosion in 2195 Al-Li Weld (4043) After 2 Hours

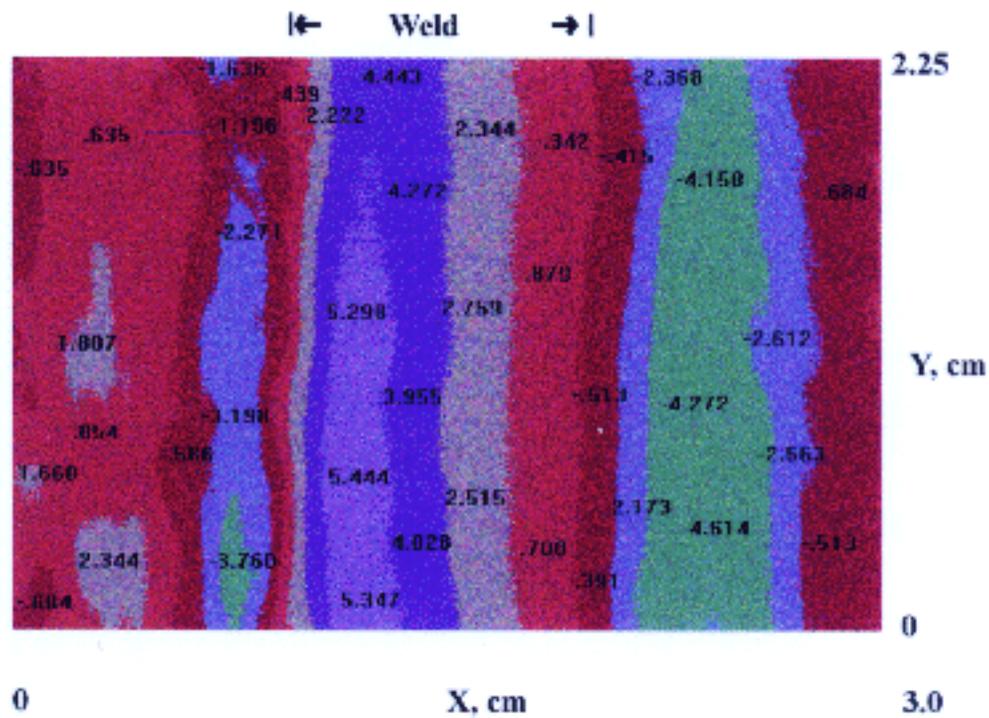


Figure 7. Localized Corrosion in 2195 Al-Li Weld (4043) After 3 Hours

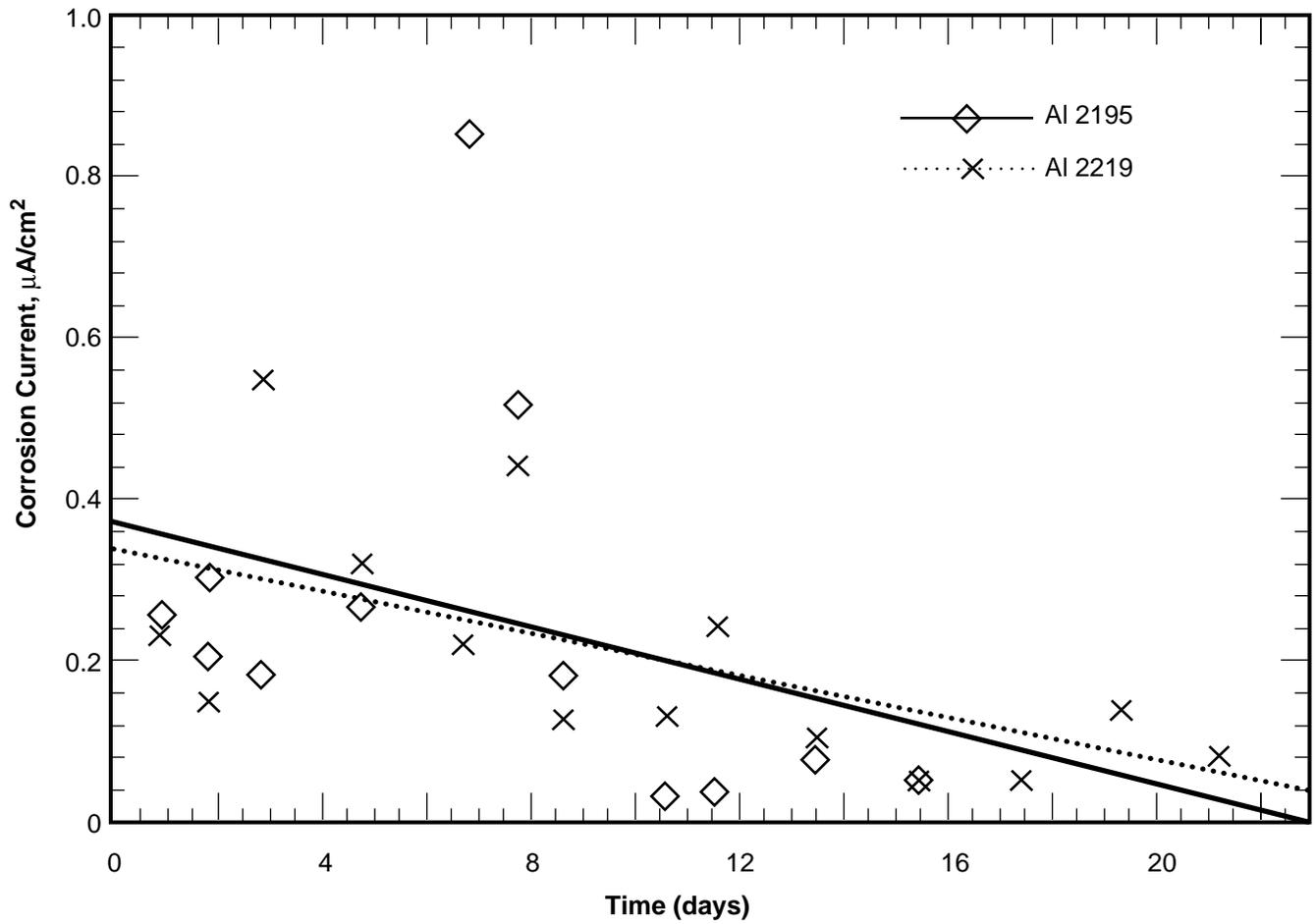


Figure 8. 2219 Al and 2195 Al corrosion current as a function of time, 3.5-percent Na-Cl (general corrosion).

REFERENCE

1. Walsh, D.W.: Unpublished results.