

DIRECT IMAGE PROCESSING OF CORRODING SURFACES APPLIED TO FRICTION STIR WELDING

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ABSTRACT

An in situ process for visually locating corrosion is presented. The process visually displays image differences obtained by subtracting one digitized image from another. The difference image shows only where changes have taken place during period between the recording of the two images. Changes are due to both corrosion attack of the surface and concentration changes of dissolved corrosion products in solution. Indicators added to the solution assist by decorating sites of corrosion as diffusion and convection of the dissolved products increase the size of the affected region. A study of the initial stages of corrosion of a friction stir welded Al alloy 7075 has been performed using this imaging technique. Pitting potential measurements suggest that there was an initial increased sensitivity to corrosion. The difference image technique demonstrated that it was due to a reformation of the passive film that occurs with Zn containing Al alloys which occurs preferentially along flow protected regions. The most susceptible region of the weld was found to be where both limited deformation and thermal transients are produced during welding.

INTRODUCTION

In situ studies of corrosion offer many advantages over post exposure measurement in determining the consequence of specific events such as transient pits, changes in the environment, or the addition of an inhibitor. In these and related problems it is often difficult to correlate the occurrence of and changes in corrosion from a series of

multiple measurements. Hence, there has been a growing emphasis on direct observations using scanning techniques to locate and monitor corrosion sites on surfaces and other in situ methods.[1,2] However, corrosion occurs at what appears to be random sites, and the detection of early events is limited because of the time required to scan an extended area. To overcome this limitation, more rapid methods are being sought to reduce the time required to locate early sites of corrosion. We are reporting on an investigation using imaging methods to rapidly identify sites of surface changes with the intention of automating the location of the sites for more detailed investigation using electrochemical scanning techniques or increased magnification.

The location of corrosion is assisted by the products of corrosion that rapidly diffuse into the surrounding solution, changing its composition and increasing the size of the affected volume even when the corroded site is sub-micrometer in size. The use of indicators that respond to the concentration changes greatly assists the location of corrosion by producing a color change [3-6] or fluorescence [7,8]. However, mass transport by convection from the corroding site also dilutes the concentration change and the response of the indicator. Gels have been used to prevent convection and increase the concentration change and indicator response. However, the addition of an indicator or limiting convection may accelerate or alter the sequence of events and change the susceptibility to corrosion, and there is a need to qualify the results with unencumbered procedures.

A technique for visually locating corrosion is being investigated. It consists of an automated comparison of surface images and display of their differences. The method is of particular help during the early stages of corrosion where the changes are limited, but also after considerable corrosion where the presence of corrosion products makes it difficult to determine whether corrosion stops or continues. The location of the initial stages of corrosion of a friction stir welded Al alloy is given as an example of an application of the technique.

EXPERIMENTAL

A programmed computer was used to control the image acquisition and processing. Color images were continuously collected using a digital camera mounted on a microscope. Two displays were presented on the monitor, the real image and a difference image. The difference images were obtained by digital subtraction of the real-time image from a previously acquired image, amplification of the difference, and offsetting of the result against a grey background. The difference image showed only the changes that occurred in the period between the recording of the previous image and the real-time image. One major advantage of the approach is that very small changes can be located and monitored over very short periods of time. Without the subtraction the monitoring of changes is extremely difficult, as the details of the image itself create a "noisy" background that camouflages the changes taking place.

Plates of aluminum Alloy 7075, 6.5 mm thick, were stir welded. Details of the process have been presented elsewhere. [9,10] Sections perpendicular to the weld were studied. The cross sections were abraded down to 600grade emery paper and then etched by applying a 0.1 M NaOH solution to bring out the region of the unaffected plate.

A container was constructed with the weld as part of its base. Generally only half the weld was exposed. The edges of the weld were masked off with transparent tape (3M Type 5.) The tape also covered two plastic supports on both sides of the weld in the same plane as the cross section being studied, enabling the tape to form the base of the container. A 25 mm square transparent acrylic resin plastic cylinder was positioned around the exposed area and glued to the tape. The weld was viewed through an optical lid placed on the cylinder. A salt bridge to an auxiliary electrode and a silver wire reference electrode passed through the lid. The container was completely filled with 0.05 M NaCl solutions containing 1% of a wide range (Fisher) pH indicator so there was no air gap present between the solution and the optical lid. The immersed optical lid reduced difficulties caused by the curvature and movement of the air/solution meniscus.

After adding the solution and recording the open circuit potential, the sample was potentiostatically controlled. Repeated potential ramps were used to determine the apparent pitting potential of the specimen and locate these susceptible areas on the sample. The ramp rate was 1mV/s and a criteria of $>15 \mu\text{A}$ was used to reset the potentiostat to a potential of -900mV, at which point and the ramp was repeated.

RESULTS AND DISCUSSION

Image Difference Analysis

Figure 1 shows an application of the imaging technique. The transparent tape used to mask the exposed area is most easily seen along the tops and bottom of the images in Figure 1. Figure 1a shows a dark area to the left. This area was produced by the NaOH etching. Within this area there are lighter roughly circular areas, which surround sites where localized corrosion occurred during the initial open circuit exposure.

Prior to polarization, the open circuit potential was around $-770 \text{ mV}_{\text{Ag}}$. Images shown in Figure 1a and b were recorded at -864 , and $-819 \text{ mV}_{\text{Ag}}$, close to the start of the potential ramping. On visual observation there are no discernable differences. However, digital subtraction of image b from a resulted in the difference image shown in Figure 1c, where corrosion sites are clearly located. They appear as white spots with some showing comet-like tails due to pH indicator changes. All the tails were in the same direction and resulted from solution convection, which is generally seen even in the confined volume of the 25 mm container. In contrast to the gray scale in Figure 1c, the original color of the difference image showed the comet tails were green close to the spots and changed to red with distance from the corrosion site. The amount and hue of the color change is a function of the subtraction parameters and the times the real images were taken. The red color was due to a decrease in pH to <4 , the lower limit of the pH indicator. The green was produced by the first image having higher red intensities than the same areas in the second image, so the result of subtraction is a lower red intensity in the difference image, which is perceived by the human eye as a green color. It should be noted that the color of the difference image represents relative changes in pH as a function of time, rather than absolute values of pH. The green color of the tails became the white color shown in the figure when the image was converted to a greyscale representation for publication.

Figure 2 shows a difference image taken during the third scan. Here the first image was taken before the anodic current had increased, the second while the anodic current was increasing. When corrosion was in progress the sites were very dark, possibly due to diffraction of light in the concentrated solution around the sites. When corrosion stopped, the sites were longer dark. At times bubbles coming from the site also appear dark, but these were intermittent occurrences. Additional processing of this image showed pH changes around the corrosion sites associated with a limited period of diffusion. Here the difference image showed the site as dark spots in contrast to that seen in Figure 1. Hence the white or dark spots offer a way to determine the chronology of the different corrosion sites even without the addition of a pH indicator.

The above analysis demonstrates a number of different inductions of sites of corrosion. Circles in Figure 1*b* have marked the indicated sites of corrosion taken from Figure 1*c*. One site is clearly above a taped area. The cause of this indication is not known for certain. It could have been due to crevice corrosion penetrating under the coating, but post exposure examination of the sample showed no evidence of crevice corrosion under the tape. Another possibility was the presence of a particle floating in the solution. The movement of these particles is often seen in the solutions and care must be taken to eliminate all particulates within the solution, on the sample, or on other components in contact with the solution.

Locations of Corrosion Susceptibility

The corrosion scenario that accounts for the observation in Figure 1 is associated with open circuit corrosion from adding the chloride solution followed by the application of a more negative potential. The corrosion was terminated by the applied potential, but the changes in solution continued to take place and spread away from the cathodically protected corrosion site.

Figure 3 shows a series of pitting potential measurements. The first five scans show a clear trend of increasing pitting potential indicating decreasing corrosion susceptibility. The fifth to tenth scans show very similar pitting potentials. This behavior suggests that the location of corrosion could be significantly different if the exposure conditions were different. A single continuous exposure would initiate at the more susceptible sites and corrosion could continue at these sites once initiated. However, if exposed to a periodically aggressive environment the location or number of the sites would change. The traditional approach of relying on single tests followed by post test observations would make it extremely difficult to assess the susceptibility of the different corrosion sites. In addition, in situ imaging has suggested a rather unexpected cause for the increased apparent susceptibility.

Figure 4 shows the location of all the sites detected using the difference imaging technique observed on open circuit exposure and during the ten pitting potential measurements. During the open circuit exposure there were about 11 sites of corrosion around the tape suggesting a form of crevice like corrosion, 3 sites in the weld nugget, and 4 sites in the dark area etched by the NaOH. The first scan produced 3 sites adjacent to the tape, 4 in the weld nugget, and 6 in the etched area.

The increased susceptibility during the first scans was mainly due to a type of crevice corrosion. It was not a true crevice but a region of restricted flow adjacent to the tape. This type of behavior has been observed with iron [11] and Zn containing Al alloys. [12] More interestingly, the Al-Zn alloys show only temporary intense activity as the passive film is modified [12], unlike Fe where the breakdown leaves a continuously active surface. The sensitivity to corrosion is only temporary, which, once developed, is lost. These metals are particularly sensitive to attack of the passive film when the corrosion product concentration increases, and the pH decreases, due to an initiation event and dissolution. Following breakdown of passivity on the freely exposed surface, both diffusion and then convection are unrestricted. The critical concentration for pit propagation is then lost and the event is only metastable. When the event occurs adjacent to the tape, the tape offers sufficient protection for propagation to continue. [5,11] The greatest protection against dilution of the corrosion product is along the corner where the tape and the metal meet. This is where passivity is most likely to be undermined by the most concentrated solution. With Zn containing Al alloys this action is extremely sensitive to any form of restricted mass transfer, and the transient attack will even spread along 600 mesh (~15 μm) abrasion scratch lines [5]. The local cell of transient activity can be seen to propagate along scratch lines leaving behind a darker, more resistant passive film.

The difference imaging method showed that the corner crevices were susceptible at open circuit and during the first few polarization scans, which offers a partial explanation for the lower apparent pitting potential. The corners became active during the early scans, but once the passive film adjacent to the tape transformed, the sensitivity was exhausted. Nevertheless, there were also sites in the weld nugget which were active only during the first few scans that added to the lower potentials. Sites in the well etched area where continuous corrosion of the stir welds would take place remained active from the first exposure until the end of the series of exposure measurements. A more detailed investigation of the structure of the weld showed that the location of the susceptible area was where both limited mechanical deformation and heating had taken place during welding. Nevertheless the synergism between the lower degrees of heating and deformation may have acted to produce the susceptibility that remained the area where corrosion started and continued to remain active.

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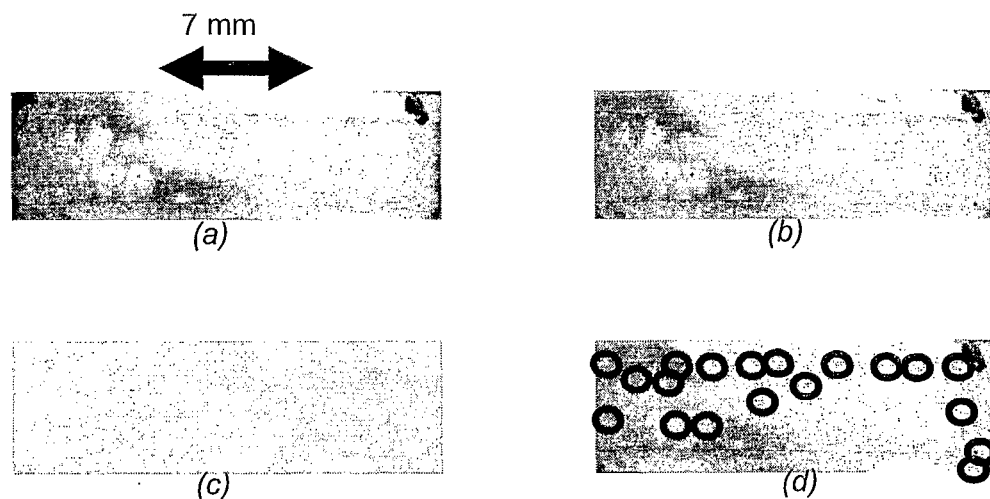


Figure 1. Digitized images and a processed image of Alloy 7075 taken at the start of potential scanning. Image (a) and (b) were taken 55s apart. The locations of events are clearly seen in the processed differences of the images in (c). Image (a) is again shown in (d) with the location of the corrosion events marked by black circles.

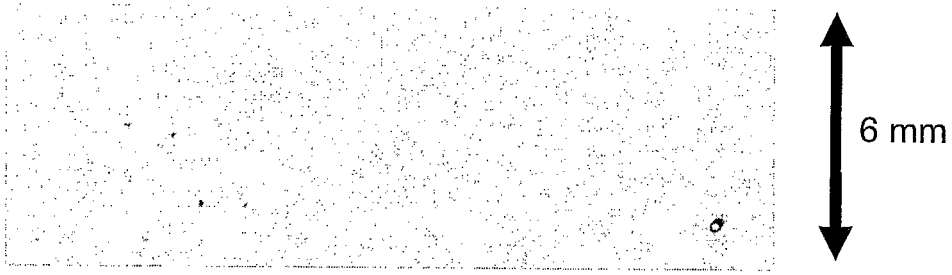


Figure 2. A difference image taken during the third scan showing sites of localized corrosion during the increase in anodic current.

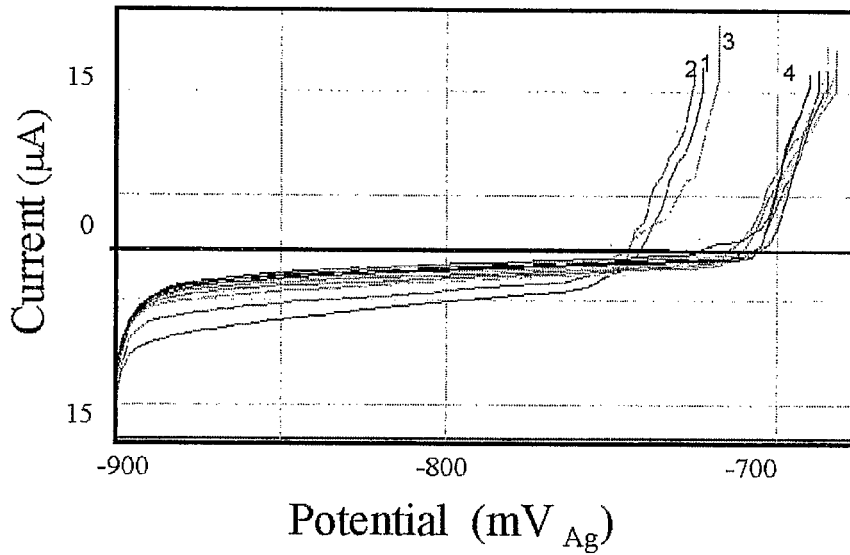


Figure 3. Repeated polarization scans at 1mV/sof the weld region shown in Figure 1 in 0.05 M NaCl.

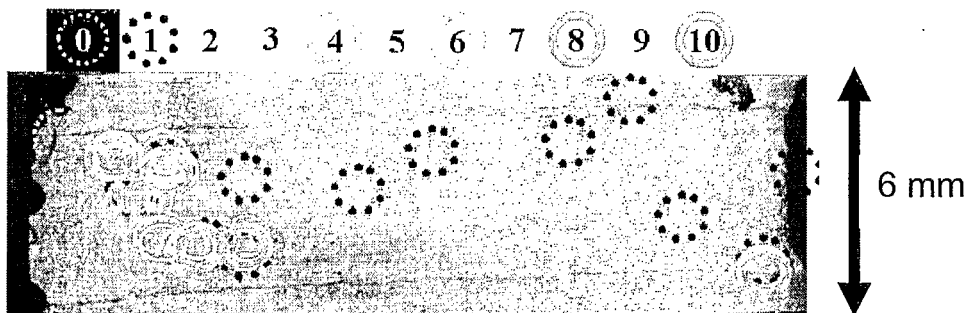


Figure 4. Sites of corrosion located from difference images. Time order is indicated by '0' following open and '1-10' during polarization scans. The background image was obtained prior to adding the chloride solution.