FINAL REPORT

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Alan M. Shipley, President
Applicable Electronics, Inc. Forestdale, MA 02644
amshipley@capecod.net www.applicableelectronics.com

Title: Non-Invasive Techniques to Study Local Passivity Breakdown of Metal Alloys in Aqueous Media.

Summary

Little is known about the basic mechanisms of passive oxide breakdown, repair, and localized corrosion of metals. A non-invasive instrument and methods have been developed to study local events and mechanisms that initiate passivity breakdown and subsequent corrosion of metals in aqueous media. The “difference viewer imaging technique” (DVIT) is a rapid, real time, non-invasive assay to study metal surfaces in corrosive solutions. It has a spatial resolution of less than 10.0 μm (1cm x 1cm sample, 1000 x 1000 pixel CCD) to observe initial corrosion processes of the order of seconds. DVIT is a software-controlled video microscopy system and methods to collect and analyze pixel changes in video images. These images are recorded from a digital CCD video camera and frame grabber package using visible light for illumination. The DVIT system detects changes in video images that represent initial corrosive events that lead to passivity breakdown and re-passivation on metal surfaces in situ. This visual technique is easy to use and apply. It compliments other metal surface measurement techniques and can be used simultaneously with them. DVIT has proven to be more sensitive in detecting changes than scanning microelectrode techniques. DVIT is also much easier than other methods to apply and operate. It has the further advantage of providing a real time image of the entire metal surface under study instead of waiting for a microelectrode to scan a number of data points over a sample then plot the results.

This project has fulfilled all specifications as outlined in the Department of Energy solicitation responsible for this grant application and award and exceeded a number of the specifications. Applicable Electronics, Inc. now has a marketable instrument and software package available for sale now. Further development of the system will be ongoing as driven by customer needs and discoveries.

This technology has immediate applications in corrosion labs to further study corrosion. It will also be useful to test coatings on metals as an industrial laboratory assay tool. The software can also process any timed series of digitized images to extract new information. Processing astronomical image data is another possible application for the software component. We also intend to apply these methods to biological research scenarios where it will be useful. Imaging extra-cellular proton flux around plant roots is currently being planned as a student project.

Discussion

We know that the refractive index of the solution just above the metal surface at corrosion sites changes due to ion concentration changes prior to passivity breakdown and also after breakdown from the dissolution of metal ions into the solution.

It is extremely difficult to detect and monitor small changes that occur in a visual image over a considerable period of time due to the obvious limitations in human observation, perception and concentration. The average viewer begins to discern changes in images only after a substantial amount of change has occurred in a relatively concentrated region. Corrosion of a metal surface typically occurs over a relatively broad area and may even regress in some areas such that the observer is completely unable to detect any alteration of the surface whatsoever. Thus, this project has successfully developed a needed technology for enhancing changes that occur in a visual image over time to enable detection by an average human observer.

New developments in CCD camera technology, computer memory, and bulk data storage and computer speed have provided the necessary technology to allow development of such an instrument. And methods that rely on digitized images for detection of micro scale events that before were hidden from the investigator.

Photo of DVIT System

The DVIT video microscopy system was designed around an Optem Zoom 70 video scope with a 2/3X video lens and a 2X auxiliary lens, a PULNIX TMC1000 package (1000 x 1000 pixel CCD and a National Instruments PCI-1428 frame grabber card) in a DELL OPTIPLEX PC with an Advanced Illumination Technology #CF1000 programmable light source with filter wheel and a #9010B adjustable, white L.E.D. 8 point ringlight and an I/O Tech DAQ 2000 A/D board connected to a Radiometer Voltalab model PGZ 402 potentiostat.

Proper illumination is essential. Evenly distributed, non-glaring illumination is preferred. Reflections from the solution surface and/or debris in the solution create artifacts in the video images. The solution meniscus is also critical. A large surface area of solution is best for reducing visual effects produced by the air/water interface.

The design of the chamber holding the metal sample under test is another major consideration. There are two basic chamber designs used. One is for viewing a sample looking down onto the sample surface from above (Figure 1a) and the other by direct use of a reflective surface glass beam-splitter in the solution to view a sample on its side. (Figure 1b)

typical experimental setup

Figure 1 (a). Chamber design for viewing a metal sample from above. Note holes to accommodate a counter electrode and a reference electrode from a potentiostat.

Figure 1 (b). Chamber for viewing a metal sample placed on edge. Gravitational effects on the dissolution of metal ions in the solution become more apparent.

The chamber, zoom scope and video microscope are mounted to a vibration isolation table (TMC Corp., Peabody, MA) to eliminate any mechanical disturbances and covered by a an aluminum Faraday cage to minimize electronic noise and any spurious room light reflecting into the sample/solution area.

Difference Viewer Software

The software and process algorithm has been developed using LABVIEW (National Instruments) software development package. The Difference Viewer software controls the video imaging hardware, the image acquisition, A/D recording and the light source with filter wheel.

The pixel changes that occur in the time interval between a chosen reference image subtracted from a later image are displayed on the PC monitor against a gray background (Figure.2).

Figure 2 shows a copy of the software screen.

The upper left image is a real-time image of pure Al and a gel containing a wide range pH indicator. The upper right image is the difference or processed image and is a result of a subtraction for the color planes between the source (real-time) and the

background image (time period previous to real-time image), the result is an image of only changes that occurred between the images.

Using a chemical pH indicator in the solution magnifies the area around the corrosion site because the pH drop around the corrosion site diffuses into the bulk solution and the using a gel in the solution prevents convection which in an aqueous solution washes away the low pH regions.

Figure 3. These images show a real-time (a) and a processed image (b). The basis of the software program is a video subtraction algorithm developed for viewing previously recorded video data to discern specific sites on the sample that change with time. This gives a clear display of changes with time.

Figure 4. The processed image depends on settings of two control bars shown above.

The Difference Offset and Multiplier adjusts the grey level and the gain of the processed image display and enhances any changes due to corrosion that occur after subtracting a background image.

Figure 5. Bringing up the A/D window displays data (e.g. from a potentiostat.) Current and potential data controlling the metal sample are displayed on a graph coincident with the real and processed images to provide temporal correlation between the image changes and the electrochemical activity.

(a)

(b)

Figure 6. Corrosion of pure Al in a gel with 0.5 M NaCl with a wide range pH indicator. (a) is the image of the sample after a period of corrosion. (b) is the processed image subtracted from an image taken two minutes earlier. The processed image clearly shows changes that took place during the two minutes and the location of four pitting sites can be seen due to the low pH shown by the indicator in the gel.

Initial tests were run with a wide range pH indicator as this approach has been shown to identify sites of corrosion. Figures 6 a and b show an experiment with pure Al and a gel containing a wide range pH indicator. Figure 6a is a real image of the specimen and it was very difficult to locate where the corrosion took place when only a little corrosion

had occurred. However, the processed image in Figure. 6b clearly shows four sites of corrosion where pitting was taking pace. Most of the sites repassivated with time while new sites activated. A number of pits showed they reactivated as the same site reappeared with time indicating the nature of pitting of Al. Other features in Fig 6b were due to changes in the gel that was drying due to exposure to room air with low humidity.

This sample provides a good indication of the sensitivity and spatial resolution of this technique. In Figure 7a and b, below, the source and processed images are shown side by side. A 160 μm square region with two adjacent active sites is highlighted in both the source and processed images, and a 3D profile, Figure 7c, of each of the color planes in the processed image is shown. The two active areas are separated by approximately 50 μm , yet the peaks in the red and green color planes are clearly visible. The presence of peaks in two color planes is due to the fact that the absorption color of the pH indicator is part way between the center wavelengths of the color filters manufactured onto the CCD sensor. The intensities of the pixel values in each of the red, green, and blue planes can be used to determine the intensity and absorption color of the pH indicator dye. By calibrating the absorption color and intensity of the pH indicator with known sources, it is possible to transform the processed images into very high resolution pH maps.

(a)

(b)

(c)

Figure 7c. Spatial resolution demonstrated during corrosion of pure Al in a gel with 0.5 M NaCl using a wide range pH indicator (same conditions as Fig. 6). The region enclosed by the green square in the source image (a) and processed image (b) was evaluated to obtain a 3D profile of the three-color planes from the processed image as shown in (c).

(a)

(b)

Figure 8. Al alloy AA2024 in an aqueous solution with 0.5 M NaCl and no gel or pH indicator. (a) shows a real image taken at about 0.5h with oblique illumination. (b) processed image indicating the locations of bubbles. These experiments were dominated by the appearance of bubbles coming from the pits.

Figure. 8 shows a real image and a processed image taken about 0.5 h after immersion. The white spot in 8b indicates the presence of a bubble than can also be seen in Fig. 8a. The black spot in 8b was where a bubble was present when the background subtraction image was recorded. The bubble dislodged from the surface before 8a was recorded leaving a negative image that appeared as a black spot.

(a)

(b)

Figure 9. A 13% Cr 2%Mo stainless steel alloy in 0.4 M FeCl₃ solution after about 0.6 h.

An experiment with stainless steel is shown in Fig. 9. The 13% martensitic stainless steel was very susceptible to crevice corrosion under the transparent tape. Figure 9a shows the real image, Fig. 9b the processed image of the sample after immersion for about 0.6 h during which time crevice corrosion took place along the tape. This can be seen at the black areas along the tape. The processed image, Figure 9b, was obtained by subtracting an image taken 2 minutes before that in Fig. 9a. Here black lines are seen. The thickness of these lines arises from the increase in size of the crevices. In other words they are a measure of the penetration of the crevices under the tape in two minutes. This demonstrates the ability of the visual assay to detect specific dissolution kinetics.

Fig. 10a shows a corroded Fe sample after about 1 h with oblique lighting. Fig 10b shows the processed image. It is interesting to note that the sample shows evidence of pitting corrosion and in the lower area corrosion has spread around the pits. However by processing the image and comparing it with an image taken 2 minutes earlier it is immediately clear that very little growth of the pits had occurred. The changes that took place were predominantly caused by the corrosion product in solution probably due to ferric hydroxide precipitation. The demarcation line due to the edge of the tape suggests that changes were also due to general corrosion of the lower left area of the exposed sample.

Fig.10. The corrosion of Fe in a 0.5 M NaCl solution after about 1 h. (a) Shows a real image taken at about 0.5h with oblique illumination. (b) Shows a processed image indicating the locations of bubbles.

Experiments with abraided type 304 stainless steel also showed crevice corrosion but to a much lesser degree. Fe on the other hand showed pitting which then slowly expanded over the surface.

Figure 11. Aluminum alloy 7075-T6 exposed to air saturated 0.5 M NaCl.
 (a) Background image recorded after 10 minutes, (b) real-time image after 13 min
 (c) difference image obtained on digital subtraction image a from image b, amplification of the difference and displaying on a grey background

Figure 12. The PC monitor display during review of the images during the reduction of a thermally grown oxide on Cu in pH 8.4 0.05 M $\text{Na}_2\text{B}_4\text{O}_7$. The Cu was exposed to a temperature gradient producing a range of oxide thicknesses. (a) background image

recorded at α , (b) real-time image recorded at β and (c) difference image obtained on digital subtraction of image a from image b, amplification of the difference and displayed on a gray background.

The following images are of a titanium sample in a sodium bromide solution. Sample is scanned with a potentiostat. It shows the location of a new pit forming during the second pitting potential scan. The real image shows the location of the new pit (upper right) and all the inactive pits formed during the first scan.

(a)

Background Image
at open circuit after the first scan

(b)

Real Image
at 2 V during second scan

(c)

Difference Image
shows location of a new pit during the second scan

Figure 13. Pitting of Ti in 0.01M NaBr

System Development

The software development was the major part of the Phase II project. Since we were using a bundled package from two different vendors sold by another vendor, there were hardware and software issues that had to be worked out along the way. Once dependable and repeatable performance was established and good data was being collected, it set up a continuous loop of experiments and data analysis, software/hardware changes/additions to speed things up or make things more user-friendly followed by more experiments and so on went the development of the methods and the instrument. One major hurdle of development was handling the very large data files accumulated while doing experiments and processing them with the software. There were some iterations of improvement of data transfer efficiency that also evolved as the PC technology market introduced new mass storage devices to solve such issues.

The hardware development went side by side with the software. Working out such issues in the optics such as the right mounting arrangement, machining of parts and the modifications (and some minor repairs) were ongoing.

The methods of magnification, illumination of the sample, kind of chamber and experimental geometry to use are dependant on the sample being measured and the type of experiment. Settling on a basic marketable platform that can be easily applied and adapted to use became the main goals at the conclusion of the project. We now have a marketable instrument and software package that is well documented.

Team Members

It must be noted that the team members doing this project have a very good chemistry and are able to do things quickly and efficiently enough to produce a very well done product in the end. Dr. Isaac's work regarding the theoretical foundations for this technique initiated this project. His laboratory at Brookhaven was the perfect location for system development. Mr. Ken Sutter, a senior member of the BNL support staff was superb in his support for the project. We enjoyed a very fine research environment to accomplish the project. Eric Karplus, president of Science Wares, Inc. designed and directed the software development based on available technology. The software is the heart of the DVIT system and Science Wares, Inc. has provided services and software beyond expectation. In particular, Mr. Hugh Popenoe, the programmer/engineer at Science Wares, Inc. was invaluable to the project. We are all continuing DVIT development with Dr. Hugh Isaacs at Brookhaven Labs.

Two undergrad mechanical engineering students, Alonzo Haughton (Stoneybrook, Long Island, NY) and Robert Poole (UMASS, Dartmouth, MA) were employed part time for this project. Two PhD students, Mae Looi and Ruoshuang Huang have also worked on this project at Brookhaven Labs. Mae Looi did part of her thesis work on the DVIT. Jennifer Hurley, (UMASS, Dartmouth, Mech. Eng.) is now working with AEI equipment doing her master's thesis work.

Working with the students has been a rewarding experience for everyone. Through this project AEI has made affiliations with UMASS Dartmouth faculty to help them develop and establish a corrosion course at the university utilizing non-invasive methods of study.

Work Plan Completion

Not all of the proposed research in the Phase II was completed. After working with two cameras (task 8) and various optical devices and attachments to try 3D imaging, we discovered limitations in our optics and equipment that would require a substantial investment in time and money to advance. It was decided that the scope of such work was beyond the limits of our current resources.

The use of different color illumination (Task 6) was also decided against mainly because there are newer technology 3 chip CCD cameras available now, but they are also very expensive (\$15-20K). Newer CCD technology would greatly reduce the time needed for software image processing algorithms that would be necessary with the CCD cameras we now have. Using a digital monochrome CCD (used about \$3K) to build an RGB image would also create more programming issues. Since we are a small company (two full time employees, two part time) we must focus our time and resources on the instrument we have now, which is powerful new tool. Further development of the system will be funded via sales of DVIT systems and by contracts with customers for special system modifications. All other tasks were completed with successful results.

Further Development

Applicable Electronics, Inc., Science Wares, Inc. and Brookhaven National Labs continue their association. We are working with Dr. Hugh Isaacs to push scientific discovery with the DVIT system. We have installed two DVIT systems at Brookhaven for Dr. Isaacs' laboratory to use and we continue support of the systems. One system will stay at Brookhaven as long as it is useable there and the other will serve visiting students doing projects. However, we may move one system to other labs for student projects if BNL does not have any planned projects for its use. Both of these systems are comprised of the equipment acquired through this SBIR grant. Since scientific publication is the best advertising for this instrument and methods it is the major part of our activity to promote its use scientifically which makes it more acceptable to industry.

Conclusion

DVIT is a novel, non-invasive, real time method to record visual changes on metal surfaces in solution. It gives us a new tool to further study the initial events that lead to passivity breakdown of metals. It is a rapid assay for corrosion testing that may replace the traditional salt spray test used in some corrosion studies. It is easy to use with little training and less time consuming than scanning microelectrode techniques. It can compliment other methods of research. The "Difference Viewer" software can also process digitized video images from other techniques that are taken in a time sequence.

DVIT can be easily combined with other non-invasive methods (SVET: Scanning Vibrating Electrode Technique and SIET: Scanning Ion-selective Electrode Technique). DVIT combined with a scanning microelectrode system and a potentiostat can record both local and global data simultaneously.

Through the course of this project, methods have been developed to use and apply the system experimentally. DVIT has just been introduced to the science world and there will be a lag between now and popular acceptance as a scientific tool and method. Then there will be another lag to be accepted as an industrial assay for corrosion.

Brookhaven Science Associates has applied for a patent for this technology and methods together with Applicable Electronics, Inc. and Science Wares, Inc. Hugh Isaacs, Alan Shipley and Eric Karplus are the names on the patent. All have signed over their patent rights to their respective corporations.

REFERENCES

1. H. S. Isaacs, J. B. Lumsden, A. Haughton, A. M. Shipley, H. Popenoe, E. Karplus, in *Corrosion and Protection of Light Metal Alloys* R. G. Buchheit, R. G. Kelly, N. A. Missert, B. A. Shaw, Edts. The Electrochemical Society **PV 2003-23** 2003.
2. R. H. Huang, C. J. Lui, H. S. Isaacs in *Third International Symposium on Pits and Pores: Formation, Properties, and Significance for Advanced Materials*, P. Schmuki, D.J. Lockwood, Y.H. Ogata, M. Seo, H. S. Isaacs, Edts., The Electrochemical Society, in press.
3. *A patent has been applied for and is pending* U.S. Patent Application, Patent Serial No. 10/713,809.