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OTEC Heat Exchanger Program: 2013 Annual Report

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OTEC HEAT EXCHANGER PROGRAM

ANNUAL REPORT

Prepared For

HAWAII NATIONAL MARINE RENEWABLE ENERGY CENTER

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SUMMARY

Makai has performed a complete run through of their in-situ pit measurement test procedure. This method combines photographic imaging, ultrasonic inspection, and laser profilometry to provide an encompassing picture of the pitting phenomena. The comparison of photographic imagery and ultrasonic data provides insight into pitting formation, growth and passivation rates. If properly calibrated, photographic imaging could potentially be used to quantify pitting corrosion. It was shown that ultrasonic technology could be used to detect the small scale pitting corrosion that concerns OTEC heat exchangers. Ultrasonic inspection allowed for the measurement of pit depth and the rate of deepening in-situ. The pit depth behavior was more complex than previously anticipated. Rate of pit deepening trends could not be established with the limited amount of data. The accuracy of these measurements was compared to the final processed sample using a laser profilometer. The comparison revealed a depth bias between the ultrasonic and profilometer instruments. This bias could be attributed to the different measuring technologies or calibration error in the instruments. The ultrasonic instrument could be measuring corrosion below the surface that is obscured to the profilometer. Destructive testing of a pitted sample could provide insight into the difference in measured pit depths. The profilometer and ultrasonic instrument both provide important insight into the pitting and are valuable complementary technologies. With further research and calibration we will be able to use this ultrasonic technology to measure rate of pit deepening in-situ with confidence.

1. INTRODUCTION

Over the past two years Makai Ocean Engineering, Inc. has completed the design and construction of a heat exchanger test facility and corrosion laboratory at the Natural Energy Laboratory of Hawaii Authority (NELHA). The long term goal of this facility is to provide heat transfer performance, corrosion and biofouling testing of heat exchangers in order to develop heat exchangers for use in commercial size Ocean Thermal Energy Conversion (OTEC) Plants. The heat exchangers are the heart of an OTEC plant: They are the single most expensive component, and the most critical relative to the overall efficiency of the plant. A 100 MW OTEC plant envisioned by Makai would house over 200 individual heat exchangers, each larger than a 20’ shipping container. Small changes in heat exchanger performance will have immense economic consequences, and any failure from corrosion or fouling would be catastrophic to the development of a billion dollar OTEC plant.

Early in the planning for the heat exchanger test facility, the subject of corrosion based on alloy selection, fabrication methods and operational parameters became important points of discussion. Makai together with industry heat exchanger developers Lockheed Martin, Chart Energy & Chemicals and Fives Cryo realized that inadequate information existed to make informed design decisions concerning materials and manufacturing methods for an OTEC evaporator or condenser. Aluminum was chosen as a baseline for corrosion testing because of several factors: 1) low cost of the material, 2) multiple options for fabrication, 3) high thermal conductivity and 4) relatively good corrosion resistance based on prior research. Material selection was largely based on the previous study by Argonne National Laboratory (“Aluminum Alloys for OTEC Heat Exchangers” by C.B. Panchal et al), which was funded by the Department of Energy (DoE) from 1983-1987. This study also provided preliminary information regarding the relative performance of manufacturing joints. Makai has expanded this study to include additional materials and fabrication methods, introduced new testing to study the effects of varying seawater flow rates, and installed representative samples of actual OTEC heat exchanger prototypes. Additionally, Makai is working with Professor Lloyd Hihara at the University of Hawaii under a DoE funded study to determine the performance of ceramer coatings on aluminum in deep seawater. The results from Professor Hihara’s work in the development of these coatings are promising, and may prove to be a good solution for the corrosion protection of aluminum heat exchangers.

2. TECHNICAL DISCUSSION

Makai began performing corrosion tests at NELHA in 2009 using warm surface seawater and cold seawater drawn from depths of 3000 feet and 2200 feet. Approximately 1500 samples, divided equally between warm and cold seawater, are currently undergoing tests to compare the corrosion resistance of 6 different aluminum alloys. Many of these samples have been immersed for a 4-year period; however, samples are continuously added as new design concepts emerge. The testing includes evaluation of joining methods such as brazed aluminum, friction stir weld and TIG welded assemblies, as well as the relative performance of electro-polished surfaces. Testing is being conducted under different flow regimes, including stagnant conditions and several flow velocities.

2.1. BASICS OF ALUMINUM CORROSION

Aluminum corrodes in two ways: uniform corrosion and localized (pitting) corrosion. Uniform corrosion is a relatively slow reduction in metal distributed across the entire surface in contact with seawater, much like one sees on a rusting steel plate exposed to a mild marine environment. Pitting corrosion, in contrast, is an unpredictable, sudden and rapid attack of the metal at a single point on its surface. Pitting corrosion essentially ‘drills’ a hole in the metal at a rate of up to 0.05 mm per day. If the pit passes through the 3 mm wall of an OTEC heat exchanger, it would be a catastrophic failure. Unlike steel, aluminum alloys submerged in seawater develop a protective oxide layer which actually reduces the rate of corrosion. Therefore, the rate of corrosion is largely dependent on the concentration of dissolved oxygen in the water and decreases over time as the protective oxide layer develops. For instance, Aluminum 5052 has a uniform corrosion rate of about 0.12 mm per year on the 5^{th} day of exposure in warm surface seawater. By the 50^{th} day, the corrosion rate is one-tenth of that. This is because the oxygen-rich, warm surface seawater builds the protective oxide layer and quickly reduces the rate of corrosion. In addition to reducing the uniform corrosion rate, this protective oxide layer serves as a deterrent to pitting initiation sites. In deep seawater, the oxygen content and temperature is low, and the protective oxide layer forms much slower than in warm water. While the warm water samples build a significant layer in the first 50 days, the cold water samples require years to build a protective oxide layer that is still inferior to the warm sample. In this time, pits may have developed.

2.2. TRADITIONAL METHODOLOGY

Makai’s traditional corrosion measurement methodology includes electrochemical methods as well as weight loss measurements. Weight analysis and electrochemical measurements both assume an average rate of metal loss over the entire sample’s exposure period. While electrochemical measurements provide an instantaneous rate of corrosion, this is only accurate if there are no pits forming on the surface. Wall thickness loss calculations using weight measurements are similarly affected by this bias. Furthermore, weight analysis requires a sample to be removed from the test, and chemically cleaned to remove the corrosion product before being weighed. This provides a single data point of weight loss during the test period *for that particular sample.* In order to characterize the weight loss of the aluminum samples over time, many samples are required, each of which is removed from the test at different exposure intervals. This is a standard method to determine the uniform corrosion rate. This method requires many samples, statistical data analysis, and many man-hours of hands-on labor that increases the potential for errors. Overall the costs are high to obtain only uniform corrosion rate data. Nothing is revealed about the rate of pitting corrosion.

2.3. NEW METHODOLOGY

During the first year of corrosion testing, it became clear that the corrosion behavior of aluminum cannot be thoroughly studied using the current measurement techniques alone. Our objective in this study was to develop a new technique for measuring pitting growth rates in order to better understand the differences between various alloys and manufacturing processes.
Makai has developed several ideas for accurately measuring the growth of pits in-situ, which will allow us to take multiple measurements of a single sample without removing it from the test rack. In addition, Makai wants to automate the process in order to reduce human error and allow for a much larger test. For example, counting individual microscopic pits manually is a very tedious process which is better suited to a computer. To achieve this goal a combination of technologies has been implemented into pit measurement method: photographic imaging, ultrasonic inspection, and laser profilometry.

3. METHODS AND RESULTS

3.1. PHOTOGRAPHIC IMAGING

The first method that Makai implemented was photographic imaging with automatic pit detection. A custom imaging apparatus consisting of two cameras mounted on a motorized stage was developed. This apparatus collected high resolution digital photographs of aluminum samples submerged in seawater through a clear acrylic window. The cameras were both Edmund Optics-5012C ½" CMOS color GigE machine vision with 5 megapixel resolution. The bottom camera was fitted with a wide field lens and the top with a high magnification lens. The wide field lens was an Edmund Optics Ultra High Resolution 12 mm lens. This lens provided a field of view of 64 mm with an image resolution of 0.04 pixels/micron. The high magnification lens was an Edmund Optics Techspec 6X compact telecentric lens with a 65mm working distance. The high magnification provided a field of view of 1 mm with an image resolution of 2.75 pixels/micron. The X and Y axes were fitted with 0.005 mm resolution encoders to provide accurate image positions. The wide field images were taken in a vertical line pattern daily. They were stitched together to create one image of the entire surface for each day. These images were analyzed and areas of interest were identified. The areas of interest could be pits or strange features and were imaged with the high magnification camera daily.

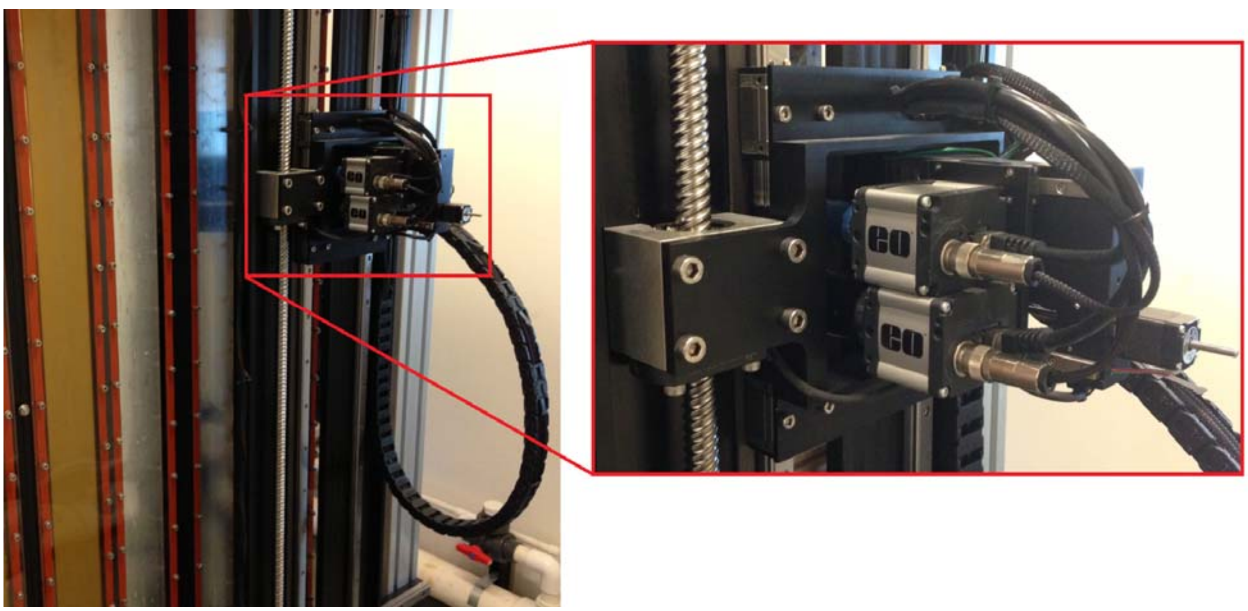


Figure 3-1: Photograph of Makai's corrosion rack with motorized X-Y-Z stage and imaging apparatus. Zoomed in view shows the Y-stage and Z-stage with the two mounted cameras. The top camera has the long microscope lens attached and the bottom camera has the short wide field of view lens.

Makai has developed an algorithm to automatically detect anomalies in time-lapse images of corroding aluminum samples using National Instrument's Labview Vision Development software. To detect anomalies in the time-lapse images, we looked at changes in the pixel intensity values over time. Local pixel darkening or lightening could signal the initiation of pitting corrosion. In order to accurately compare the intensity values of two images, they must be carefully aligned. Alignment was achieved using perspective, angular, and scale correction. Once the images are aligned, a histogram matching normalization was used to identify bright anomalies within a defined threshold. The intensity threshold was set above the standard deviation of intensity for the whole sample. In Aluminum, a pit site will become visible within a number of days depending on the alloy. To detect these rapidly developing pit sites, the algorithm compares the current day's image with the image taken several days prior. Any group of pixels that changed in intensity greater than the threshold between those days is analyzed. In order to avoid false positives, areas with less than eight surrounding pixels are disregarded. Surrounding pixels of eight or more that are touching are grouped together and considered one anomaly. These areas are recorded as points of interest to be re-imaged in high resolution. To quantify pitting corrosion over time, the daily images were compared against the image from day 1.

An aluminum alloy 2024 sample was placed in cold seawater until it developed many pits. The algorithm was able to identify the majority of these pits by the white corrosion product that was produced. The number of pits detected increased rapidly during the first three days and then began to slowly decrease as shown in Figure 3-3. The relative pitted area increased rapidly during the first three days and then continued to increase at decreasing rate as shown in Figure 3-4.

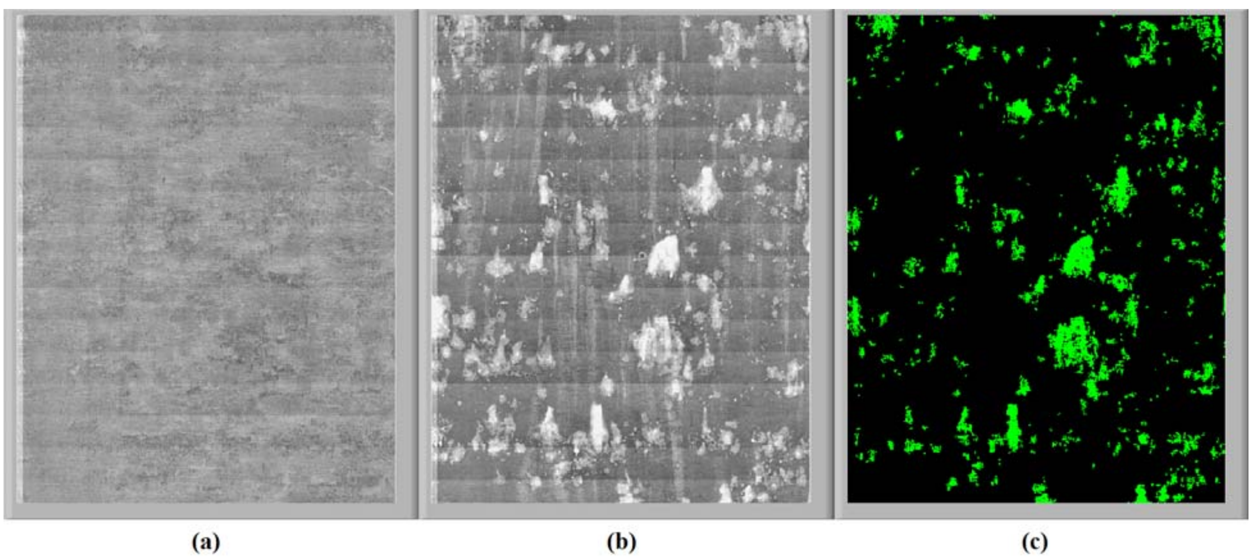


Figure 3-2: (a) Sample area of Alloy 2024 at day 1. (b) Alloy 2024 at day 26. (c) Detected pitted area shown in green

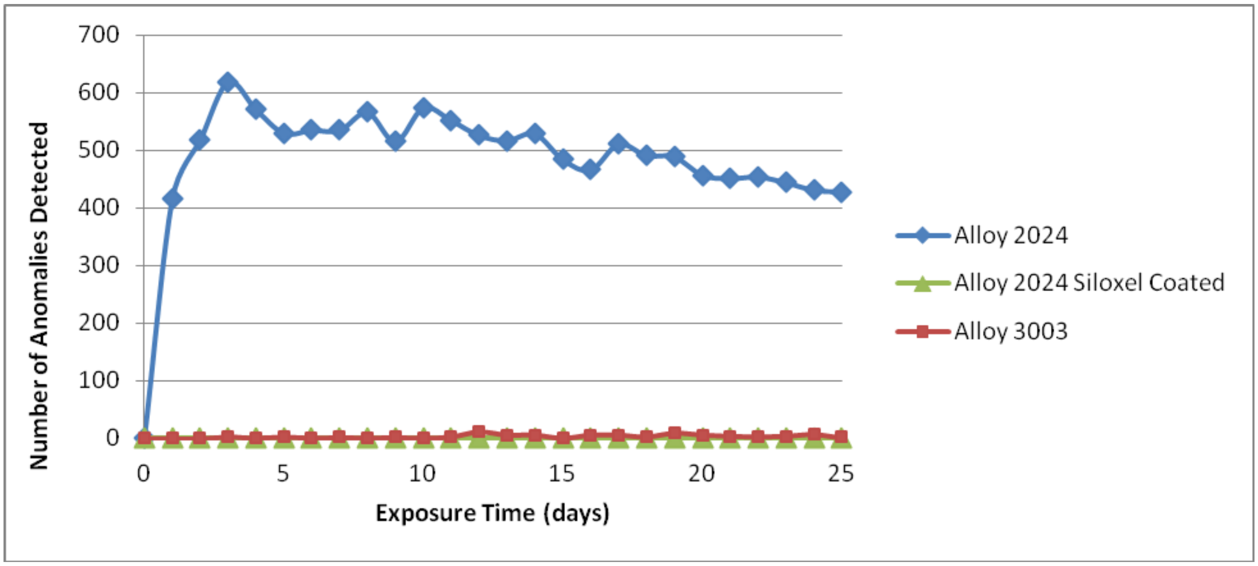


Figure 3-3: Number of anomalies detected for the three different aluminum samples

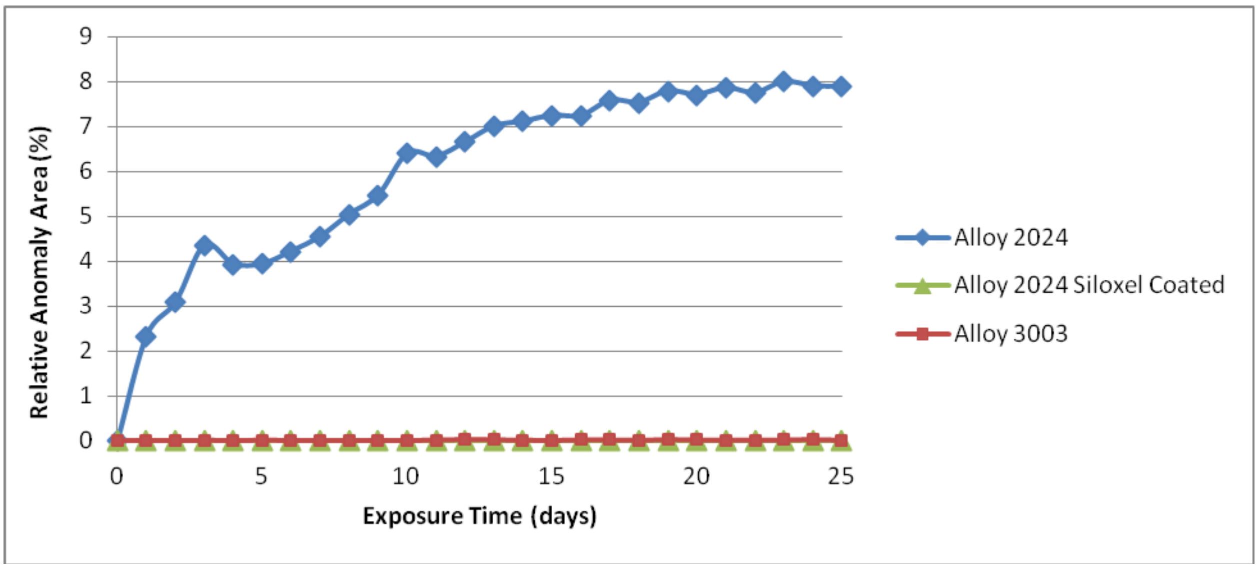
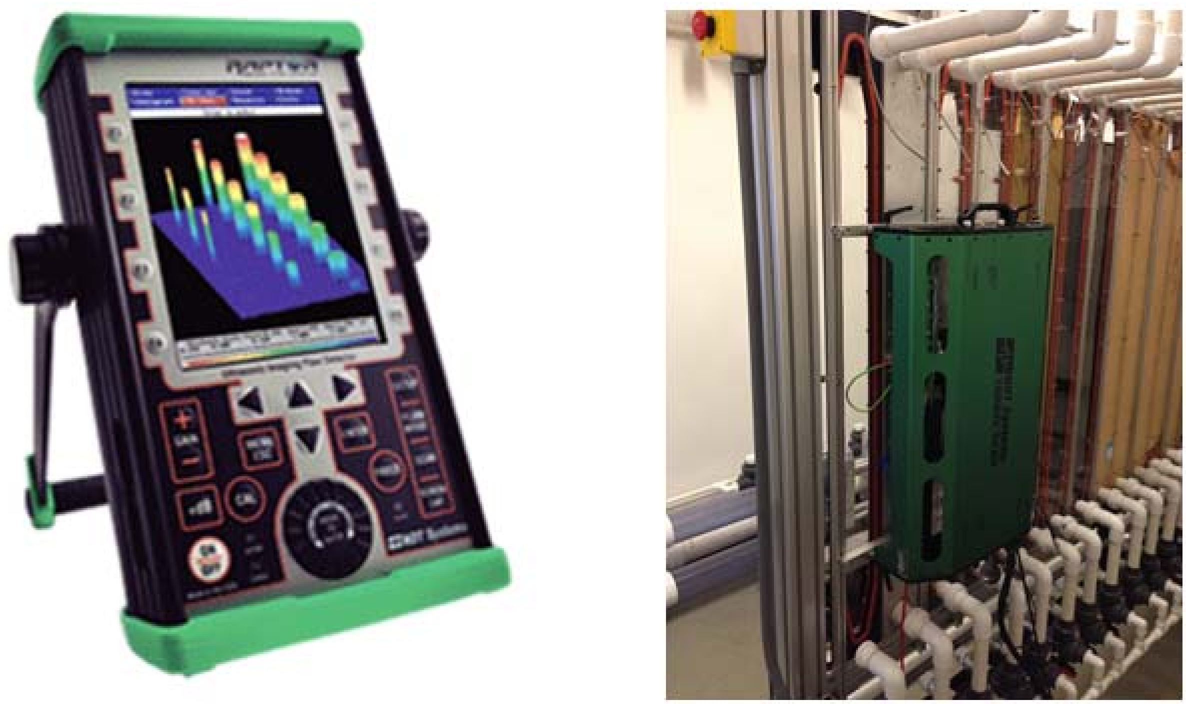


Figure 3-4: Relative anomaly area (%) for the three aluminum samples

The algorithm was successful in detecting anomalies in the sample metal surfaces. The high sensitivity of the algorithm enabled early anomaly detection so that pit initiation and development could be imaged in high resolution. Although not all anomalies become pits, it is important to begin imaging the anomalies in high resolution as soon as possible to capture the potential initiation of pitting corrosion.

3.2. ULTRASONIC

Makai has employed ultrasonic thickness gauging technology to map the pits that develop in our aluminum samples. The main goal of the ultrasonic method is to determine the rate of pit growth through the wall, without removing the sample from the test rack. This information could be used to calculate the expected life of a heat exchanger. The ultrasonic apparatus we employed was a Raptor® imaging flaw detector and a TunnelScan® motorized scanner manufactured by NDT Systems Inc. The transducer used was a D11 high resolution delay line type with a 0.250 inch element that operates at a frequency of 15 MHz. The transducer was held pressed against the sample's surface by a spring loaded yoke on the X-Y scanner. Pressurized water is supplied to the transducer head to maintain a liquid interface with the sample.



(a) *(b)*

Figure 3-5: NDT Systems RAPTOR imaging flaw detector and (b) TunnelScan mounted on the back side of Makai's corrosion rack.

An accelerated 145 day test was conducted on a 2024 Aluminum bar sample in surface seawater. The sample was scanned with a resolution of 0.05 mm x 0.05mm. The ultrasonic thickness data over time was analyzed to determined rate of pit deepening. Change in thickness was determined by subtracting the first day's thickness profile from the subsequent day's thickness profiles. A uniform reduction in sample thickness could be attributed to the process of uniform corrosion, sensor drift, or a combination of the two. The change in thickness due to pitting corrosion (pit depth) was defined as the total change in thickness minus the uniform change in thickness. Pits were identified and quantified using a threshold depth. Any group of adjacent points deeper than the threshold was considered a pit. Pits were identified in each day's depth profile, recorded and tracked through the life of the test. If two pits merged, this new larger pit would maintain the same identification number as the deeper of the first two pits. The record would show the deeper pit as continuing to exist and the shallower pit and ceasing to exist. The rate of pit deepening and pit widening is shown in Figure 3-6 and Figure 3-7. In this experiment, pits exhibited many different behaviors. Some pits deepened quickly in the first week and then slowed to a much more gradual deepening rate. Similarly, the pitted areas grew rapidly in the first 20 days of exposure then leveled off. At approximately 100 days, there was another rapid deepening stage and area growth stage. Many new pits were identified on day 138. Soon thereafter many of these newly identified pits merged into fewer larger pits by day 145.

The ultrasonic data was mapped and overlaid onto the photographic image data. A representative set of images with ultrasonically measured pit depth contours overlaid is shown in Figure 3-8. In the first 10 days many small dark circles form on the surface of the sample as seen in the photographs. During this time only 3 pits were detected with the ultrasonic flaw detector. Most of these dark circles seen in the photos would not turn into deep pits. The largest ultrasonically detected pit in the top left quadrant exhibited white corrosion product in the photographs. The other two ultrasonically detected pits did not exhibit significant corrosion product in the surrounding areas. By day 99 a large clump of corrosion product remained over the largest and deepest ultrasonically detected pit. There was some corrosion product near the other ultrasonically detected pits. At day 138 large clumps of white corrosion product were visible over most of the ultrasonically detected pits except for one. By day 145 all the ultrasonically detected pits had visible white corrosion products over them. The deepest pits appeared to have the largest clumps of corrosion product over them. It appears that the presence of white corrosion product indicates an active pit. More study is required to investigate this.

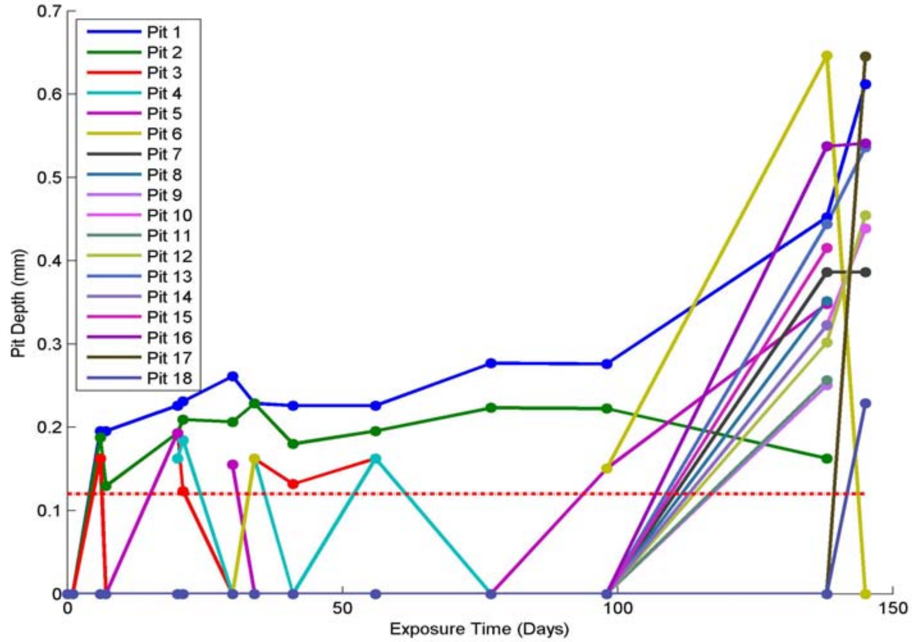


Figure 3-6: The ultrasonically measured depth of 18 tracked pits on the 2024 Aluminum sample submerged in surface seawater for 145 days.

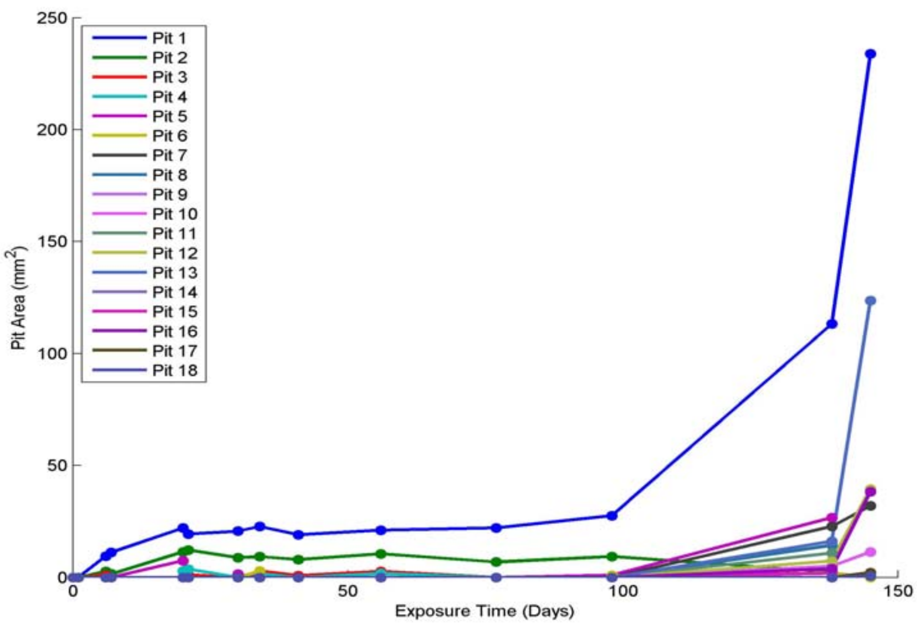


Figure 3-7: The ultrasonically measured area of 18 tracked pits on the 2024 Aluminum sample submerged in surface seawater for 145 days.

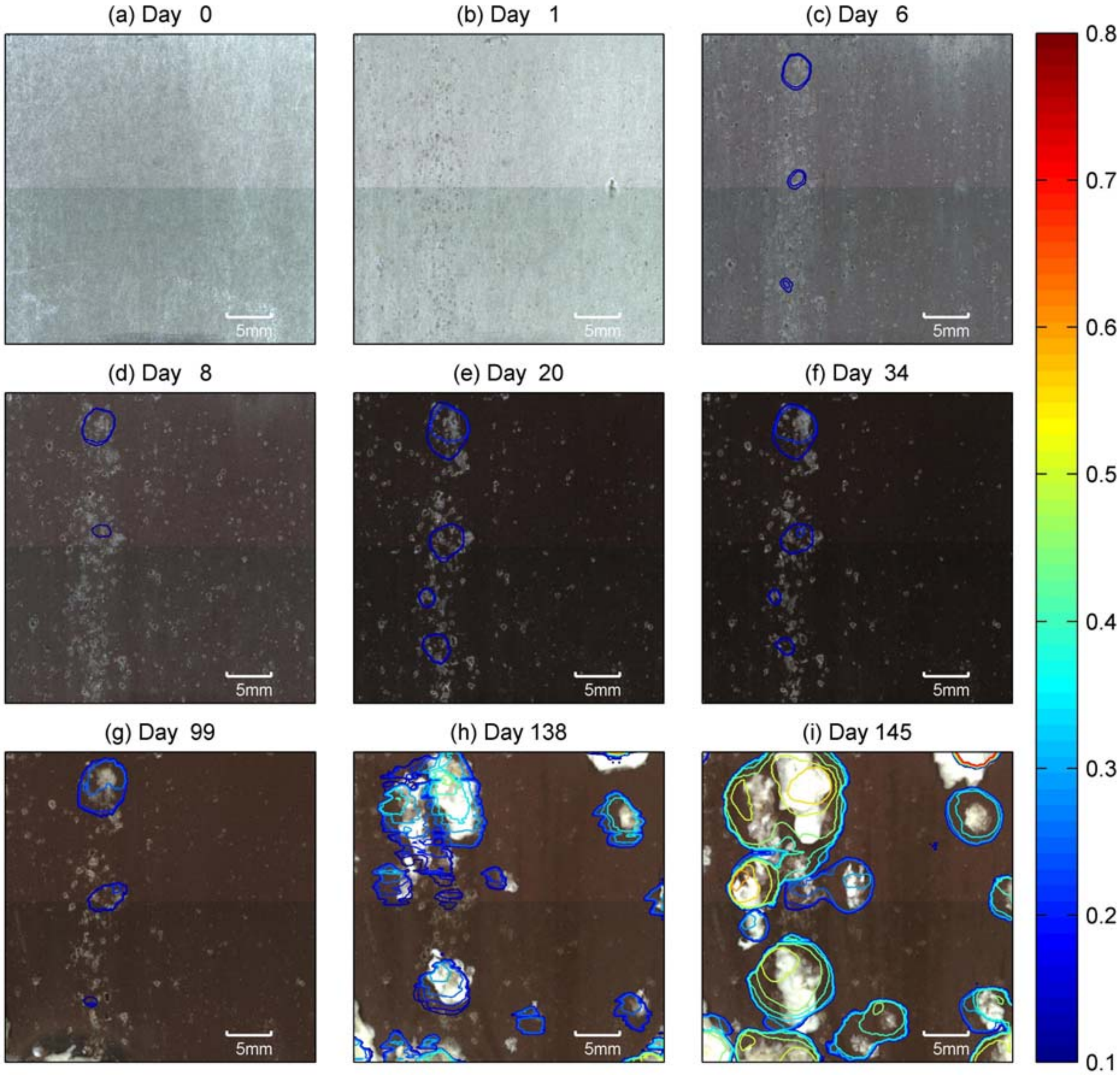


Figure 3-8: Front view photographs of the 2024 Aluminum sample's area of interest after indicated days of submersion in surface seawater with ultrasonically measured pit depth contours overlaid.

3.3. LASER PROFILOMETRY

Makai uses a laser profilometer to measure the final surface profile of their samples. After the test on a given sample is complete, the sample is removed from the seawater test rack and cleaned for final measurement and analysis. The accuracy of this instrument is an order of magnitude higher than the ultrasonic scan (0.001 mm compared to 0.03 mm). This final measurement is used to validate the data taken from the ultrasonic equipment.

The ultrasonic data from the last day of the 145 day accelerated test was mapped and overlaid onto the profilometer data from the last day. A profilometer depth color map with ultrasonically measured pit depth contours overlaid is shown in the Figure 3-10 (a) below. Two cross sectional views of the depth data allow for comparison between the ultrasonic and profilometer measurements in Figure 3-10 (b) & (c). It can be seen from the color map and the cross sections that the ultrasonic instrument measured the pits slightly deeper and substantially wider than the profilometer. Thirteen pits identified in the profilometry data were associated with six pits in the ultrasonic data. In the ultrasonic data, pits appear wider than they actually are and overlap occurs. The depth of the deepest pit within its cluster in the profilometer data is compared with its associated pit in the ultrasonic data. The ultrasonic instrument measured the pits to be deeper than the profilometer did as shown in Figure 3-9. The ultrasonic instrument was able to detect pits as shallow as 0.20mm. In this experiment we discovered that the ultrasonically measured pit depths were on average 0.18 mm deeper than the profilometrically measured pit depths. The standard deviation was 0.10 mm and the maximum error was 0.33 mm.

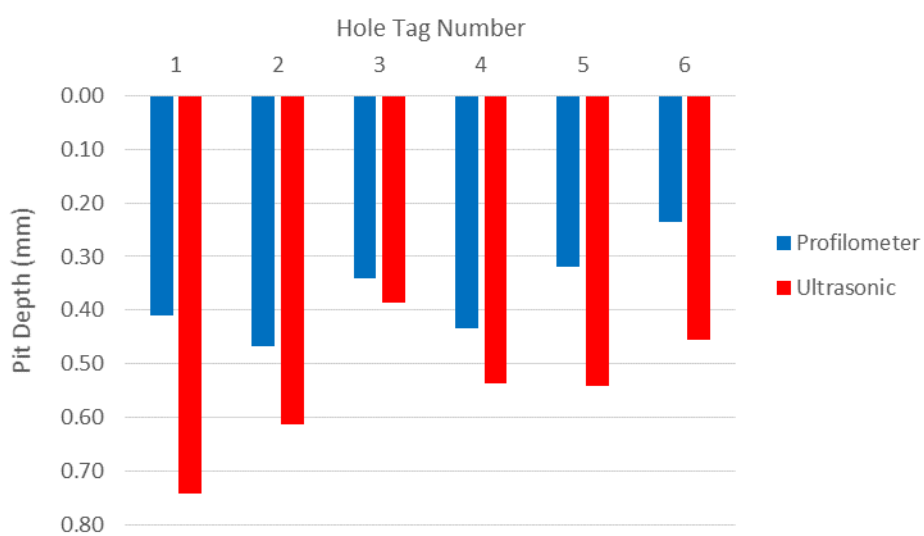


Figure 3-9: Comparison of pit depth of the 2024 Aluminum sample's area of interest after 145 days of submersion in surface seawater measured using ultrasonic and profilometry techniques.

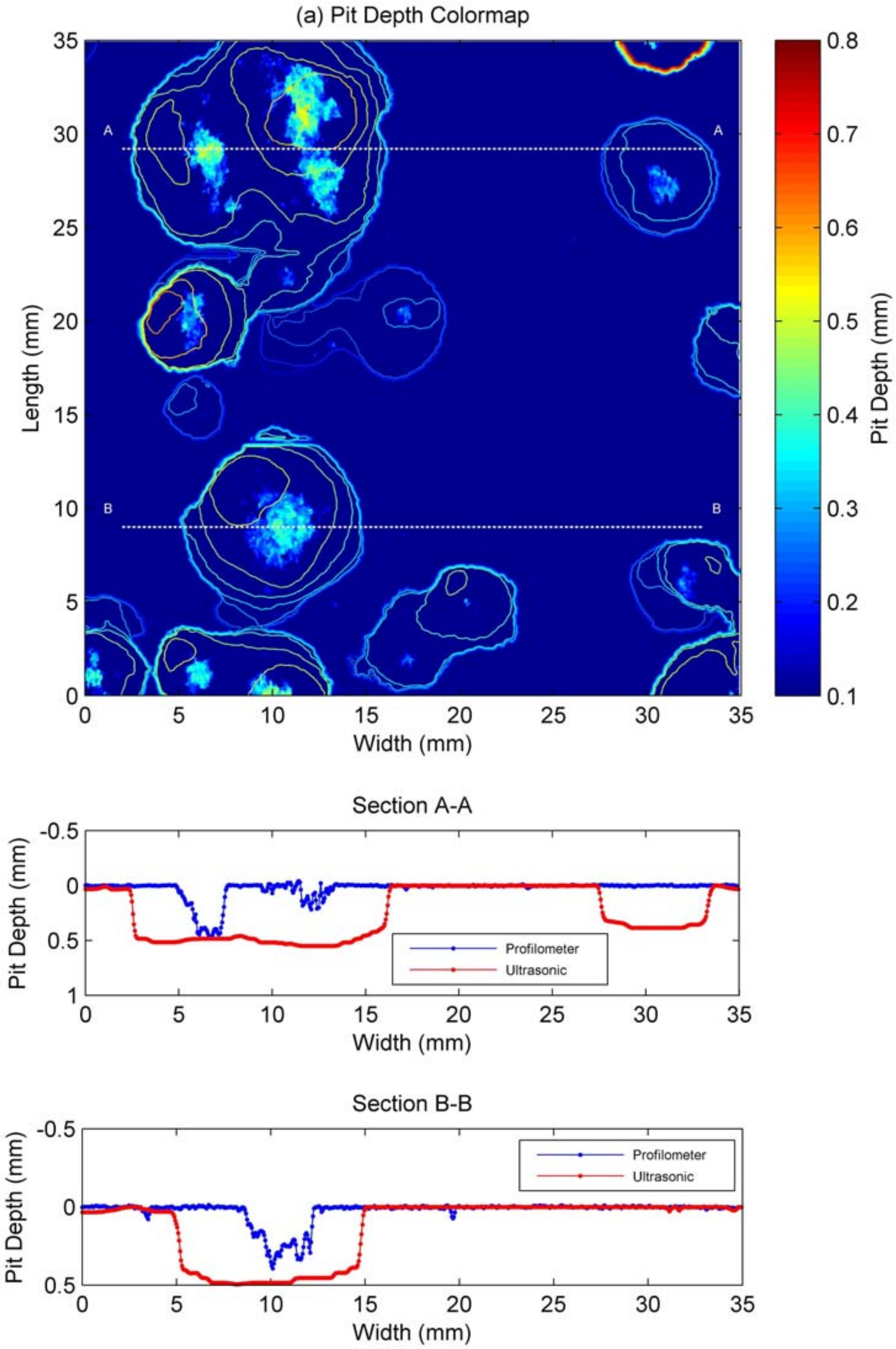


Figure 3-10: (a) Map of the 2024 Aluminum sample's area of interest after 145 days of submersion in surface seawater with profilometrically measured pit depth shown as a solid color, and ultrasonically measured pit depth contours overlaid. Both data sets use the color bar scale. (b)-(c) Cross section views showing depth data as measured with the profilometer (blue) and ultrasonic (red).

4. CONCLUSIONS AND DISCUSSION

4.1. PHOTOGRAPHIC IMAGING

Photographic imaging provides important information about the changes that occur on aluminum surfaces during seawater immersion for extended periods of time. Changes in surface reflectivity, color, and morphology can help us better understand the chemical processes that are occurring. The most practical use of the imagery to Makai is the observation and characterization of pitting corrosion. Corrosion pits in aluminum become covered with white, voluminous and gelatinous pustules of alumina gel AL(OH)_2. The comparison of imagery and ultrasonic thickness data in this experiment verified that all actively growing pits were covered with white corrosion product. The visual image comparison algorithm implemented in this effort was successful in detecting the white pustules and quantifying them by number of pits detected and a pitted area. However the algorithm did have some disadvantages that limit its practicality. Precise image alignment was required to correctly compare images and detect variations. The algorithm also required significant manual adjustment and was not able to handle significant changes in sample surface color. During the effort of pit detection and quantification in the ultrasonic data, a new pit tracking algorithm was developed. This new algorithm applied to the photographic imagery should perform significantly better than the original. A fixed intensity/color threshold would be used to identify the white pustules. This will require only a one-time camera exposure calibration at the beginning of the test and make the algorithm much less sensitive to surface color changes. It will also reduce the algorithm's sensitivity to precise image alignment. Pit pustules will be identified independently in each daily image, then their position and areas are compared with pits from previous days. Pits that maintain a set percentage overlap with previously detected pits are considered the same pit and tracking is continued. Pits with no overlap are considered newly detected and added to the list of tracked pits. This algorithm will track these pits and maintain a record of their area as a function of time. Pustule height could potentially be measured using the change in focal positions of the high resolution camera. Average and maximum pustule volumes could be estimated and provide insight into the rate of rate of pitting corrosion. Since pustules are much bigger than the underlying pitted cavity, a method to estimate actual cavity size would be highly desired. With the collection of more photographic, ultrasonic, and profilometric data, a relationship could potentially be established that relates pustule size with pit cavity size. This could provide a high-speed in-situ pit measurement alternative to the ultrasonic scanner.

4.2. ULTRASONIC AND PROFILOMETER DEPTH MEASURMENT

Ultrasonic gauging was selected as a rapid in-situ method for quantifying pit deepening rates in aluminum alloys. This technology is the industry standard method for non-destructive measuring of corrosion. OTEC heat exchangers have thin walls between 1 – 3 mm thick and any pit breach could cause a shutdown of the entire plant. The unique challenge in this situation is the ability to detect very small and shallow pits. This pit detection size range is pushing the boundaries of current ultrasonic technology and requires thorough validation. To validate and identify the limits of this technology, we designed and manufactured an aluminum block with drilled holes of various different diameters and depths. It was found that scanning the calibration block ultrasonically at higher spatial resolutions led to the detection of shallower holes. The shallowest hole detected was 0.48 mm at a scan resolution at 0.025 mm. Although less shallow holes were detected at lower scan resolutions, measured hole depth remained consistent. The ultrasonically measured hole depths were on average 0.36 mm shallower than the profilometrically measured holes depths. The standard deviation was 0.20 mm and the maximum error was 0.51 mm. This skewed depth error distribution could possibly be attributed the hole bottom shape, or to a calibration error in either the ultrasonic or profilometer instruments. This calibration block had holes drilled with 118 degree point angle drill bits. The conical bottoms of these holes could be scattering the ultrasonic energy and weakening the return signal to the receiver leading to a shallower-than-expected depth measurement. The ultrasonic calibration error would most likely be due to an incorrect speed of sound value. This speed of sound has to be determined experimentally for each material by comparing the ultrasonically measured thickness to a known thickness.

The accelerated 145 day corrosion test was the first comparison we performed between ultrasonic and profilometer data on a pitted aluminum sample. Figure 3-10 reveals the ultrasonically measured pits to be slightly deeper and substantially wider than those measured with the profilometer. Due to the nature of the ultrasonic technology, the pit cavities appeared much wider than they actually were. Since penetration of the heat exchanger wall is our primary concern, pitted area is not as important as pit depth. Scanning at a spatial resolution of 0.05 mm, we were able to detect pits as shallow as 0.20mm. In this experiment we discovered that the ultrasonically measured pit depths were on average 0.18 mm deeper than the profilometrically measured pit depths. The standard deviation was 0.10 mm and the maximum error was 0.33 mm. This depth error distribution was skewed in the opposite direction of the calibration block errors. This again raises the question of whether errors were due to bottom shape or calibration errors. The ultrasonic instrument could be measuring corrosion below the surface that is obscured to the profilometer. Since calibration is relatively straight forward; the first objective would be to re-calibrate the ultrasonic and profilometer instruments. A test should be devised to ensure that they are accurate relative to each other. One lesson learned is that ultrasonic pit depth calibration should be done on representative surfaces. A calibration block with conically bottomed holes is not representative of pitting corrosion. We recommend calibrating the ultrasonic instrument on a sample pitted with corrosion and comparing a statistically significant number of pits. Destructive testing by cutting a pit down the center would be a convincing method to verify accuracy of both the profilometer and ultrasonic depth measurements.

5. FUTURE WORK

5.1. CALIBRATE ULTRASONIC AND PROFILOMETER INSTRUMENTS

To ensure confident comparison between ultrasonic and profilometer depth measurements, both instruments should be re-calibrated. The profilometer z-axis scaling factor calibration should be verified using a step height standard. The ultrasonic thickness scaling factor calibration should be verified using a multi-step thickness gage calibration block. Several representative pits in aluminum should be measured using both instruments then destructively cut open to examine the cross-section. Examination of pit cross-sections under the microscope might provide insight as to why the ultrasonic and profilometer measure pit depths differently. This investigation could possibly reveal sub-surface pitting. The depth of the pit's cross-section could be also be measured with a micro ruler under the microscope and compared with the ultrasonic and profilometer measurements.

5.2. IMPLEMENT NEW AUTOMATED PIT DETECTION ALGORITHM

The new pit tracking algorithm that was developed should be implemented with the photographic imaging. This algorithm should perform significantly better than the original and work with many different sample types. Pits would be tracked and their area as a function of time will be recorded. Measuring pustule height by change in focal position using the high resolution camera could be investigated. If this proves to be practical it could possibly be used to estimate average and maximum pustule volumes. With the collection of more photographic, ultrasonic, and profilometric data, a relationship could potentially be established that relates pustule size with pit cavity size. This could provide a high-speed in-situ pit measurement alternative to the ultrasonic scanner.

5.3. IMPLEMENT ELECTROCHEMICAL POTENTIAL MEASURMENTS

Measuring electrochemical potential could provide insight into pitting corrosion. Corrosion potential could be compared with rate of pitting as measured with the photographic imaging and ultrasonic to look for correlations. Correlations between corrosion potential and rate of pitting would be very valuable because corrosion potential is the most practical in-situ corrosion measurement technique for large heat exchangers in OTEC plants.

5.4. TEST NEW CORROSION SAMPLES IN RACK

We would like to use our new corrosion measurement methodology to examine various aluminum alloys under consideration for OTEC heat exchangers. From our previous corrosion research we have noticed that each alloy exhibits slightly different pitting behavior. With our new measurement abilities we will be able to quantify the difference between the corrosion behaviors in the different alloys.