Development of a Stress Corrosion Cracking test approach for multi-mode measurements

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Experimentation to study stress corrosion cracking (SCC) often requires simulation of aggressive environments that include both tensile loading with simultaneous chemical exposure. This demands complex testing approaches that will benefit from multi-mode measurements to capture in-situ degradation. Multi-mode measurements aid in characterizing the nature of the reaction, quantifying the formation of corrosive products and in calculating the breakdown potential of the sample. This paper details a testing approach for the chemical aspect of SCC on aluminum samples where sample and experimental design facilitates in-situ imaging. In initial tests, 3.5 wt. % NaCl solution is applied to AA7075 for specific time frames which initiate the pitting process. The testing approach enables to produce optical microscope images of real-time reactions. Raman and microscopy measurements help capturing failure initiation mechanisms which eventually lead to crack propagation. Identification of specific Raman peaks reveals the nature of the products formed on the surface using the pre-exposure values as a baseline for the characterization. These results from multi-mode measurements can be compared to understand SCC processes with both qualitative and quantitative information. Knowledge gained can be used to design materials and processes to better withstand corrosive environments.

I. Nomenclature

SCC = Stress Corrosion Cracking
SEM = Scanning Electron Microscopy
EDAX = Energy Dispersive X-Ray Analysis
DIC = Digital Image Correlation

II. Introduction

Aluminum alloys have a wide range of applications and are commonly used in the manufacturing of aircraft components due to their light weight and high strength to density ratio. They also have excellent formability and are very easy to machine which makes them ideal alloys. Among the various series of aluminum alloys, 7xxx and 2xxx series have the most prominently used in the manufacturing of aircraft parts [1]. This paper uses 7075-T651 as it is widely used in aerospace structural components such as the wing spars of aircrafts, where a combination of high strength with moderate toughness and corrosion resistance are required [2]. While these alloys exhibit superior

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mechanical properties, they are also highly susceptible to Stress Corrosion Cracking (SCC) when exposed to environments that induce stress and corrosion simultaneously [3]. SCC occurs in two phases namely crack initiation and crack propagation [4]. The focus is set to the initiation period as it helps understand the development of crack tip and enables researchers to come up with solutions to improve the mechanical properties of the alloy. During this initiation period, mechanical stress and corrosive environment interact with each other at a localized crack region during the 'incubation period' leading to formation of pits [5]. These pits, over time interact with precipitates that exist within the grain boundaries to promote the growth of crack [6]. The purpose of this study is to develop multi-mode measurement techniques to track the initiation phase of SCC. SCC requires two different elements namely stress and corrosive environment. It is highly important to study the corrosion behavior separately and use it as a benchmark to contrast the results after the introduction of mechanical stress. This study focuses on the effects of corrosion on the surface inclusions which are known to be precursors for stress corrosion cracking [7,8]. The methods that were used in this work include Raman spectroscopy and optical images as they aid us to determine the rate of oxidation, quantify grain boundary precipitation or observe depleted grain boundary regions by tracking concentration variations. The samples are tested pre-corrosion and after 48 hours of exposure to visualize the formation of corrosion products.

III. Materials and Methods

AA 7075-T651 is a high strength aluminum alloy with zinc as the primary alloying element as shown in Table 1. Other elements such as SI, Cu, Mn and Mg affect the microstructural and electrochemical behavior of the alloy.

A. Raman spectroscopy

Raman spectroscopy is performed for high resolution quantification of local corrosion inclusion volume fractions. Oxides that emerge during the corrosion process provide specific Raman peaks in the laser-probed area which can be identified using their spectral signatures. The spectral maps are extremely useful in tracking corrosion both qualitatively and quantitatively. The location and concentration density of the products formed can be revealed through Raman spectroscopy. Corroded sample is expected to produce peaks that superposes the emission from molecular structure already present within the surface. These peaks can then be referenced and identified, and their phase volume fractions can be used to deduce the corrosion rate.

Al	Fe	Si	Cu	Mn	Mg	Cr	Zn	Zr	Ti
Bal	0.075	0.169	1.23	0.056	2.5	0.203	5.72	0.027	0.028

Table 1: Chemical Composition of the AA 7075 aluminum wires in wt. %

B. Sample and 3.5 wt. % NaCl preparation

The corrosive fluid used to conduct the experiments is 3.5 wt. % NaCl which was prepared in the laboratory using ASTM G44 standard. The pH meter device is recalibrated using different grades of deionized water and 3.5g ACS grade sodium chloride sample is added into the beaker to 96.5ml of deionized water and thoroughly stirred until the salt dissolved. The sample used for the pre-loaded experiments is of dimensions 20 x 20 x 6.35 mm^3. It was cut from a 6in x 6in plate and then polished with wet sanding paper of increasing grit size up to 10,000 grits. The surface of the sample was washed with deionized water and then cleaned with isopropyl alcohol to clear dust particles. Then 0.5ml of the3.5 wt. % NaCl solution was transferred onto the surface of sample using a graduated pipette and one droplet of Reagent Type IV deionized water was added every hour for 48h to replenish the water lost by evaporation. Deionized water is added because adding additional salt water would increase the salt concentration over 3.5 wt. %. No additional droplet of water was supplied during the last hour to let the fluid on the surface dry. After exposure, the samples are rinsed with deionized water to eliminate the hygroscopic salt products to prevent further corrosion.

C. Procedure

To set-up the sample for Raman spectroscopy, the system was recalibrated using a silicone calibrant. This affirms that the system is synchronized and able to produce peaks without disturbance as well as to account for any potential shift in the Raman spectra. The sample was then transferred to a stand under the optical lens and high-resolution

images were captured to be used as reference. Oxides may appear across an extended spectrum range. A 600 g/mm grating size was chosen to capture potential oxide peaks over an extended range up to roughly a 3750 cm^{-1} Raman shift. This is done to capture specific peaks over an extended area and this reduces the resolution between the recorded wave number. Higher resolution data is then collected once these peaks are identified in the extended range. An integration time of 20s was used to capture the oxides on the corroded samples. A 40 x 40 μm^2 map with a resolution of 1µm was adequate to capture the precipitate data and their surrounding areas to observe possible pitting.

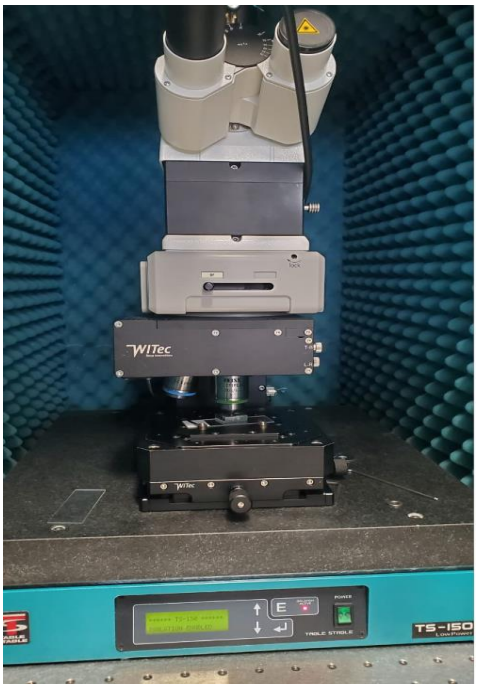

Figure 1: Experimental setup of the Raman system used for scanning AA 7075- T651 samples.

Parameter	Value
Laser Wavelength	532 nm
Calibration Sample	Silicon Calibrant
Integration Time	30 - 60 s
Acquisition Number	1
Accumulations	1
Laser Power	100% / ~15.6 mW
Objective	20x

Parameter	Value
Laser Wavelength	532 nm
Grating Size	600 gr/mm
Calibration Sample	Silicon Calibrant
Integration Time	20 s
Acquisition Number	1
Accumulations	1
Laser Power	100% / ~13.4 mW
Objective	20x
XY – Map Dimensions	40 x 40 μm^2
Step Size (X/Y)	1 µm / 1 µm
Number of Points (X x Y) (Total)	40 x 40 (1600 points)
Estimated Scan Time	33,600 s 09:20:00 (hh:mm:ss)
# of Maps per Sample (Min)	2
Total Time per Sample (Min)	67,200 s 18:40:00 (hh:mm:ss)

Figure 2: Raman experimental parameters for Raman spectral measurements for the reference sample (left) and the samples with exposure (right).

IV. Results and Discussion

The Raman spectroscopy method was able to produce spectral maps and track the evolution of oxide formation on the surface of the sample. This data of the spectra is used as baseline to come up with parameters from which hyperspectral Raman mapping can be configured. Figure 3 shows the optical image of the selected precipitate after corrosion.

The optical image shown in Figure 3 reveals the effects of corrosion on the surface of aluminum alloy as the degradation of matrix can be clearly visible. After exposure to corrosion, oxides and other corrosion products are expected to form on the surface based on the composition of aluminum products near the precipitates. Figure 4 shows the Raman peaks after 48h of exposure. The graphs show distinct peaks at 220 cm^{-1}, 320 cm^{-1} and 630 cm^{-1} which have been identified as, copper oxide products (Cu_xO) [9]. These products can be used to track the local micro-structural evolution of the material. This result can be contrasted with the results after introduction of mechanical stress to accurately detail the impact of stress corrosion cracking and how its mechanism is different from simple corrosion.

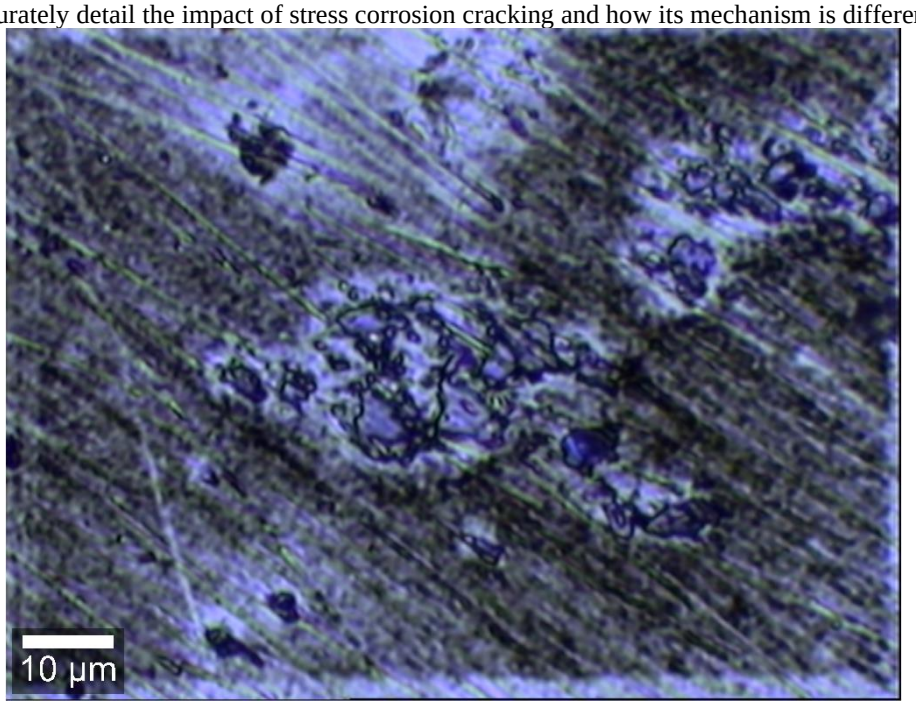

Figure 3: 50x optical image of the 48h sample after exposure to the 3.5 NaCl solution with

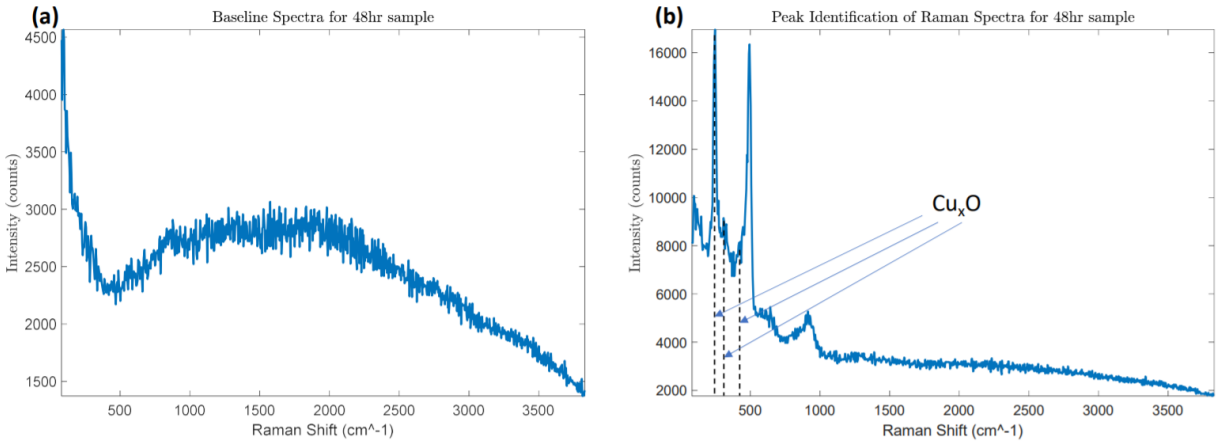

Figure 4: Raman spectra of (a) baseline spectra of the 48h sample (b) peak identification of 48h sample

V. Conclusions

The Raman scans performed in this work prove to be an important step in understanding the evolution of Stress Corrosion Cracking in aluminum alloys. Raman data can help us identify and track compositional changes of oxides formed. Raman coupled with EDAX and SEM measurements can capture the microstructural changes in pitting and inclusion sites which gives an expanded view of impact of corrosion in SCC. This can be contrasted with in-situ measurements that include mechanical loading to track material's susceptibility to SCC over time. While Raman spectroscopy provides only indirect information that helps tracking SCC, it paves way for a better understanding of crack initiation factors and can be used in conjunction with other experiment methods such as electrochemical measurements, microhigh-resolution-DIC, and X-Ray tomography, all of which can together paint a more complete picture of Stress Corrosion Cracking mechanisms.

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