

Characterizing Corrosion on AA-7075 Through Alternative Cleaning Methods and Optical Profilometry

Steven Kopitzke
Naval Air Warfare Center – Aircraft Division
48066 Shaw Rd
Patuxent River, MD 20670
United States of America

Karla De Jesus Santiago
Naval Air Warfare Center – Aircraft Division
48066 Shaw Rd
Patuxent River, MD 20670
United States of America

Rachel Black
Naval Air Warfare Center – Aircraft Division
48066 Shaw Rd
Patuxent River, MD 20670
United States of America

ABSTRACT

Recent efforts have highlighted a potential issue in the currently accepted ASTM G-1 mass loss standard as an effective means for evaluating corrosion damage on aluminum alloy 7075-T6. It was found that the use of the current standard can result in users reporting mass loss values that are inconsistent with the visual corrosion assessment, including mass gain instead of loss on obviously corroded samples. It is hypothesized that the current method of repeated immersion in acidic solution followed by mechanical cleaning is not effective at dislodging corrosion product from the pits formed on a corroded aluminum surface. To address this issue, studies have been completed to evaluate a two-step method for corrosion analysis. First, ultrasonic cleaning of coupons in nitric acid more effectively removes corrosion from the corroded surface. Second, follow-on analysis of the cleaned coupons with both mass loss and optical profilometry demonstrated that there is significant amount of corrosion information which analysis via mass loss alone will not reveal. The present work focuses on the refinement of a new cleaning protocol for aluminum and the use of profilometry to assess coupons corroded in outdoor exposure and accelerated corrosion tests.

Key words: Cleaning, aluminum alloys, pitting, optical microscopy, test methods, corrosion test

INTRODUCTION

Measuring the severity of corrosion on a specific alloy is often accomplished via mass loss using ASTM G-1.¹ These processes work well and provide high fidelity data for many materials, especially steels. However, recent internal findings and disclosures from other research groups have highlighted a potential issue with using mass loss techniques to measure the damage on some aluminum alloy surfaces.² Mass loss analysis of AA 7075-T6 coupons demonstrated extensive visual indicators of corrosion but provided

minimal mass loss measurements or even mass gain after applying the techniques outlined in ASTM G-1. Follow-on discussions with the University of Dayton Research Institute identified the following issues with the procedures for aluminum mass loss in ASTM G-1. They are, in no specific order:

- 1) The use of harsh chemicals, especially boiling phosphoric acid mixed with chromic acid, results in the aggressive removal of non-corroded material.³
- 2) The mass loss techniques do not specify how many cleaning cycles should be employed. This allows a user to continue cleaning a coupon until mass loss is observed, even if the material loss is caused by the removal of pristine material.
- 3) The use of mechanical scrubbing or shot-peening does not effectively remove corrosion product from subsurface corrosion commonly seen in aluminum alloys

An alternative method of post-exposure cleaning was developed in 2001, utilizing sonication in nitric acid to successfully remove corrosion product while minimizing the damage to non-corroded material.³ Around the same time, small scale studies had begun to reveal the importance of using optical profilometry to measure the effects of corrosion on an aluminum alloy surface.^{4,5} However, ASTM G-1 continues to be the accepted primary method for assessing aluminum corrosion damage.⁶

Based on the issues and previous research outlined above, a new method for measuring corrosion damage on aluminum substrates is required. The goal of this research is to identify the optimal method using a combination of refined mass loss techniques and optical profilometry to characterize material damage observed from non-uniform corrosion.

EXPERIMENTAL PROCEDURE

Aluminum alloy 7075 (UNS A97075) coupons were purchased from Metal Samples Inc. (Munford, Alabama) with a T-6xxx temper. The coupon dimensions were 2.54 cm by 5.08 cm by .31 cm thick with a 0.64 cm hole drilled in the middle with a unique ID code laser etched on one face of the coupon. The coupons were polished on the opposite face with P-800 aluminum oxide paper to a uniform finish ($R_a = 1.25 (\pm 0.10) \mu\text{m}$). After polishing, the coupons were sonicated in acetone and ethanol, successively, for 10 minutes each and then air-dried. The pre-exposure mass of each coupon was collected in triplicate on an analytical balance and was recorded to five decimal places.

Three different exposure conditions were selected. Twelve coupons were installed on a natural seawater spray rack at Naval Research Lab - Key West and sprayed 2 times per day, 45 seconds per spray. One set of six coupons was exposed for three months, while the other was exposed for six months. A second set of 12 coupons was placed in a accelerated corrosion chamber running GMW 14872 cyclic accelerated corrosion testing protocols. In this test, one set of six coupons was exposed for 1,000 hours while the second set was exposed for 2,000 hours. Lastly, 18 coupons were placed in a chamber running ASTM G85.A4 acidified accelerated corrosion. The exposure times for these three sets of six coupons were 100, 250 and 500 hours. All of the coupons were mounted on acrylic panels with nylon bolts and washers. The coupons were arranged in a staggered pattern in order to prevent run-off contamination from one coupon onto a lower coupon. Coupons undergoing outdoor exposure testing were installed in two vertical columns of three coupons each on a single sheet of acrylic, which was mounted on a 45° rack. Coupons undergoing accelerated corrosion testing were installed in vertical columns of three on a single sheet of acrylic, and the mounting board was installed in the chamber at a 15° offset from vertical.

After completing an exposure period, the coupons were immediately rinsed with deionized water, removed from the mounting fixture, patted dry with a Kim-wipe and left to air-dry for 15 minutes. Weighing the coupons before the 15 minutes had elapsed resulted in unacceptable variability between replicates due to residual evaporation. The coupons were weighed at the end of the drying period to determine a

post-exposure mass before cleaning. Coupons not undergoing immediate follow-on analysis were stored in a desiccator until the analysis was completed to provide protection and minimize further deterioration.

Within each exposure type, the coupons were divided into three groups. Two coupons were cleaned via sonication in ACS-grade nitric acid, another two coupons were cleaned following a modified ASTM-G1 mass loss procedure and the last two coupons were sent to a commercial third party for independent mass loss analysis. For the coupons cleaned via sonication, each coupon was sonicated for a total of 60 minutes, divided into four 15-minute intervals. In between each cleaning interval, the coupons were rinsed twice with deionized water, massed and analyzed via profilometry. For the second group of coupons, the researchers used a modified version of ASTM G-1. As stated in the introduction, it was suspected that the application of too many cleaning cycles in ASTM G-1 resulted in the unwanted removal of pristine material. In order to protect against this, only three cleaning cycles, consisting of a five-minute immersion in nitric acid followed by mechanical brushing, were used for each coupon. Like before, the coupons were massed and imaged in between each cleaning cycle. The last two coupons underwent mass loss analysis by an independent company, using a proprietary process that was stated to conform to ASTM G-1. These were only imaged once, after the mass loss procedure was completed and the coupons had been mailed back to the researchers.

Profilometry data was collected using a Keyence[†] VK-250 3D Laser Scanning Microscope with a 20x objective lens. For each coupon image, a series of individual images were captured, compiled into a single image, and analyzed in the accompanying Keyence Multi-File Analyzer[†] software. The first step of the analysis was to remove any surface tilt, a uniform effect found over the entire coupon, usually created by uneven pressure during the polishing process. After compensating for tilt, the “Volume and Area” function in the software was used to study the pit morphology. To standardize the analyses, all coupon face images had dimensions of 5.4 mm x 7.00 mm rectangle with a threshold of -1.5 μm below the surface and eliminated any pits with a surface area less than 500 μm^2 . These filters were used to eliminate any features generated due to polishing and to prevent the pit count from exceeding 3000, the highest number of pits that can be evaluated in the software.

Method validation was conducted using coupons from a separate, concurrent study. The aluminum coupons were the same alloy type, temper and size as the previously described coupons. However, these coupons were exposed with a surface roughness of $R_a = 10\text{-}13\ \mu\text{m}$ due to experimental decisions for that study. The coupons were installed on acrylic panels in the same manner as the coupons described above and were exposed on ambient, covered, and natural seawater spray (1 spray per day for 45 seconds) racks at Naval Research Lab – Key West for 119 days. Within each exposure condition, three different clear water rinse (CWR) intervals (no rinse, 1x/week and bi-daily) were applied. Mass loss analysis was completed using the nitric acid sonication technique. Follow-on profilometry analysis occurred after all four of the ultrasonic cleaning cycles had been completed.

RESULTS and ANALYSIS

Coupon cleaning and mass loss

Coupon cleaning was accomplished by sonication in nitric acid, according to the published work by Ferrer & Kelly.³ The application of four cleaning cycles was chosen based on the desire to maintain the curve fitting data analysis techniques listed in ASTM G-1. Based on the mass loss after each cleaning cycle it appears that most of the corrosion product was removed after the first cleaning cycle. However, to develop the equation for the intersecting line to calculate mass loss, the second, third, and fourth cleaning were completed to establish the equation of the second line. In addition, profilometry analysis during the cleaning process confirmed that most of the corrosion product was removed after one 15-minute cleaning

[†] Trade Name

cycle (Fig. 1) but more heavily corroded coupons could have strongly adhered corrosion product remaining through one or two more cleaning cycles. There was no evidence of corrosion product on the surface after four cleaning cycles.

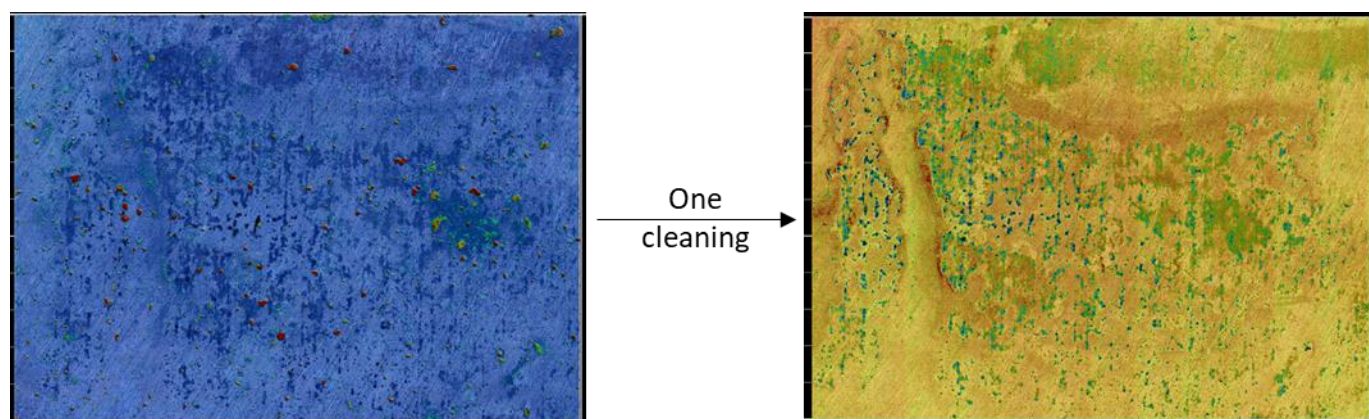


Figure 1. All corrosion products (red areas in left image) are removed after one cleaning cycle

The application of only three cleaning cycles as prescribed in ASTM G-1 was chosen arbitrarily but with the intent to avoid excessively cleaning the coupon. Post-experimentation, a review of the mass loss data showed that the rate of mass loss per cleaning cycle stabilized to be nearly the same as the coupons that were ultrasonically cleaned when examining the second and third cleaning cycles. However, both profilometry of the surface and mass loss measurements demonstrated that ultrasonic cleaning removed more corrosion product from corroded coupons.

Exposure Type	Mass loss (% mass lost)		
	Ultrasonic cleaning	Modified ASTM G-1	Difference between methods
ASTM G85.A4			
100 Hours	0.54% ($\pm 0.01\%$)	0.39% ($\pm 0.02\%$)	32%
250 Hours	1.21% ($\pm 0.04\%$)	0.74% ($\pm 0.05\%$)	48%
500 Hours	2.83% ($\pm 0.09\%$)	1.77% ($\pm 0.12\%$)	46%
GMW 14872			
1000 Hours	0.13% ($\pm 0.07\%$)	-0.04% ($\pm 0.01\%$)	178%
2000 Hours	0.07% ($\pm 0.01\%$)	-0.08% ($\pm 0.02\%$)	200%
Key West			
3 months	0.16% ($\pm 0.02\%$)	0.13% ($\pm 0.02\%$)	21%
6 months	0.26% ($\pm 0.01\%$)	0.17% ($\pm 0.02\%$)	42%

Table 1
A Comparison of Mass Loss Data from Different Cleaning Techniques

When examining the data in Table 1, a few trends become apparent. First, use of the ultrasonic cleaning method removed more material per exposure type than any other method. For coupons exposed in the G85.A4 chamber significant edge corrosion, bordering on exfoliation was observed. This was also observed to a lesser degree for the coupons exposed outdoors at Key West. Sonication while immersed in nitric acid performed two actions simultaneously. The nitric acid effectively dissolved away most of the corrosion product while the simultaneous ultrasonic cleaning removed the remaining bulk corrosion material. The use of ASTM G-1 with mechanical brushes does not have adequate bristle diameter or stiffness to successfully clean the edges of the coupons without damaging the non-corroded surfaces. Second, for coupons in the GMW 14872 test chamber, use of the modified ASTM G-1 cleaning method demonstrated that the coupons exhibited a mass gain at the end of the cleaning cycles, consistent with the findings that initiated this study. It's believed that mechanical brushing is not effective at removing corrosion product from the pits due to the small size of the pits. However, ultrasonic cleaning achieved