

Characterization of the Surface Chemistry at Corroded and Non-Corroded Sites on Aluminum Alloy 7075-T6 Samples Exposed at Coastal Locations

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ABSTRACT

Replicate samples of bare aluminum alloy AA7075-T6 were exposed at three coastal atmospheric test sites: Kennedy Space Center (KSC) FL, US Naval Research Laboratory in Key West, FL (NRL-KW), and Daytona Beach, FL. The samples were cross sections of rod stock mounted in standard two-part epoxy metallurgical mounts and wet polished with isopropanol to 600 grit finish. The samples were installed on atmospheric exposure racks and retrieved at intervals of 3, 6, 9, and 12 months. Elemental composition of baseline (non-exposed) and exposed samples were measured using a Zeiss EVO-50XP Environmental Scanning Electron microscope equipped with a EDAX Genesis 2000 energy dispersive X-ray spectroscopy (EDS) system. Pitted and non-pitted sites on each sample were analyzed for compositional elements of the alloy as well as non-compositional elements (i.e. environmentally-derived). It was determined that the deposition of elements in pitted locations on the specimens occurred at concentrations of 200% to 800% to that of major ions present in natural seawater. The deposition and concentration of these environmentally derived elements on the metal surface vary as a function of exposure site and length of exposure time.

Key words: aluminum, atmosphere, corrosion, environmental, scanning electron microscopy, energy dispersive, X-ray, spectroscopy

INTRODUCTION

Knowledge of the localized corrosion environment on a metal substrate can provide the critical link between atmospheric data and corrosion morphology and can enable the formation of a framework to predict service life as a function of environment. Over the last few decades the analytical characterization of bare metal surfaces undergoing atmospheric corrosion has improved, resulting in a more complete understanding and consideration of the environmental parameters involved. However, the corrosion processes and the role that the environmental parameters play in what is a multiphase system is rather complex involving chemical reactions and equilibria, ionic transport phenomena, and gaseous, aqueous and solid phases.¹ Various corrosion products, specific to the metallic substrates in the system, and the corrosive species present (anions, cations, acidic and basic salts, particulates, etc.) which interact with each other all vary in amounts and residence time. For the purposes of atmospheric corrosion, the electrochemical nature of the corrosion process requires the presence of an electrolyte, provided by the atmospheric precipitation or adsorption of water molecules on the surface of the metal. Adsorbed water layers, which can range from 15 to 90 atomic layers thick depending upon the relative humidity (RH), play a central role in supporting the electrochemical process.²

Researchers have reported on the role of atmospheric contaminants and the critical %RH required for atmospheric corrosion to occur on several metal substrates.³ This critical relative humidity therefore depends upon the type of metal surface, the type of corrosion products or species and particulates/pollutants that are present in the system. Also, atmospheric constituents found on metal surfaces are a function of the atmosphere itself, with sulfates, nitrates, nitrites, chlorides, carbonates, hydrogen ions, ammonium, metal ions, particulates and organic compounds commonly found in electrolyte chemistries or corrosion layers. Each of these have an effect on the corrosion processes on exposed surfaces.⁴ These result either directly from the deposition processes or from aqueous phase reactions of the deposited atmospheric constituents, whereas sulfates, chlorides and cations such as sodium, magnesium, calcium, potassium and bromine can originate either directly from the wet deposition process, from particle deposition or from aerosol reactions of the gaseous air pollutants in the aqueous phase of the adsorbed electrolyte.¹

Many investigations have been performed in recent years to clarify the role of environmental and climatic factors in the atmospheric corrosion of commonly used structural metals and coatings as well as to simulate in the laboratory their observed corrosion behavior in the field.⁵⁻⁹ It is well documented that corrosion behavior of metal substrates in accelerated laboratory tests do not correlate with the observed performance in an outdoor exposure environment.^{6-7,10,11-12}

The first step towards developing better accelerated test methods is to analyze and accurately reproduce these environments in a laboratory setting. A successful accelerated test method, therefore, would be environmentally tunable and provide accurate predictable results for any substrate with any type of protective barrier layer or coating present.

In the present work, a matrix of epoxy-mounted 7075-T6 alloy samples was exposed at three geographic locations in order to understand the role of atmospheric contaminants and environmental conditions on the corrosion and degradation of bare metal substrates. For the purposes of this manuscript, only the surface chemistries of aluminum alloy 7075-T6 specimens and analyses will be considered. The database generated from these field exposures is currently being used in the development of an accelerated corrosion test protocol on identical bare metal alloy specimens using a modified laboratory atmospheric exposure chamber.

EXPERIMENTAL PROCEDURE

Aluminum alloy 7075-T6 rod stock, 0.375 inches (0.9525 cm) in diameter was cross-sectioned and mounted in a standard 1.25 inch (3.175 cm) diameter epoxy metallurgical mount. Each mounted rod

section was wet ground to American National Standards Institute (ANSI) 600 grit silicon carbide (SiC) finish. The polished epoxy mounts were then sonicated for 30 seconds in ethanol and air dried and inspected under 25x magnification for polishing defects or gaps at the rod-epoxy interface. The composition (average weight percent) of the 7075-T6 alloy sample as determined by atomic absorption and inductively coupled plasma-optical emission spectrometry is listed in Table 1.

The epoxy mounted samples were vacuum sealed in Mylar bags containing oxygen scavenger and desiccant packets to prevent corrosive attack during storage and transportation to the exposure sites. The samples were then mounted on exposure racks at their respective field exposure sites: the Battelle Florida Materials Research Center in Daytona Beach (B-D), the NASA Kennedy Space Center Beachside Atmospheric Corrosion Test Site (KSC), and the Naval Research Laboratory in Key West (NRL-KW). The exposure period at NRL-KW started on February 2019, with the exposure rack located 226 feet (69 m) from the high water mark, facing south. The exposure period at KSC started on May 2019, with the exposure rack located 121 feet (37 m) from the high water mark, facing northeast. The exposure at B-D started on August 2019, with the exposure rack located 492 feet (150 m) from the high water mark, facing east/northeast. At each location, the mounts were exposed for 3, 6, 9, 12, 15, and 18 months from the initial deployment date. At the appropriate time, each sample was placed into a vacuum sealed Mylar bag, again with a desiccant and oxygen scavenger packet and shipped back to the Corrosion Science & Engineering Laboratory located at the University of Dayton Research Institute (UDRI). The received Mylar bag containing the sample was logged in, sample removed and identification number recorded and then re-sealed until subjected to analysis by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). This process was completed for every sample from each location for every quarter.

Table 1
Elemental Composition of 7075-T6 Rod Stock Material

Element	Average Weight %	Standard Deviation
Al	90.45	0.041
Cr	0.20	0.008
Cu	1.33	0.027
Fe	0.12	0.001
Mg	2.38	0.013
Mn	0.03	0.000
Si	0.06	0.097
Ti	0.02	0.000
Zn	5.41	0.041
Total	100.00	

Non-exposed and retrieved field exposure samples of the epoxy mounted 7075-T6 samples were subjected to SEM/EDS for image and elemental analysis using a Zeiss Environmental Model EVO-50XVP scanning electron microscope integrated with an Energy Dispersive Analysis X-Ray (EDAX) Genesis 2000 EDS system. Imaging of the metal surface and elemental data for the control (non-exposed) as well as metal composition of the field exposed metal alloy samples and environmentally-derived contaminants were determined in the “as received” condition, with no cleaning or processing. Samples were observed from an 8.5 mm working distance with a fine viewing setting as opposed to coarse. The sample would then be scanned across the surface for areas that contained pits or large amounts of corrosion product build-up as well as for areas that were void of any corrosion. For each sample an analysis was run for three different areas that contained corrosion and three different areas without any corrosion to obtain an average weight percent value for each type of area. For the metal alloy composition, each area would be analyzed at accelerating voltages specific for the alloy component¹³: 30 kV (aluminum and chromium), 20 kV (magnesium), 10 kV (zinc and silicon), and 5 kV (copper); 18 kV

for environmentally-derived elements (chlorine, sodium, sulfur, potassium and calcium), which are all major elements present in seawater.^{14,15}

After the samples had been analyzed in the as received condition, they were rinsed and sonicated in deionized (DI) water for five minutes. Following the completion of the sonication, the sample would be dried under flowing nitrogen gas and vacuum sealed again in its respective Mylar bag to be analyzed again by SEM/EDS; this allowed for the composition of the non-water-soluble and well adhered corrosion products to be determined. The SEM/EDS analysis followed the same process as previously described to obtain data for the chemical composition.

Calibration of the SEM/EDS was accomplished using high purity metal foils of Cu (99.998%), Mg (99.940%) Zn (99.999%) and Al (99.999%). Each foil was analyzed according to its associated kV value.

RESULTS

EDS Elemental Analysis – Control 7075-T6 Sample

Elemental analysis at varying accelerating voltages of a control 7075-T6 sample that had not been exposed in the field was performed to determine how closely the resulting weight% of each major element in the alloy compared to the AA/ICP values. Accelerating voltages of 5 – 30 keV were used and the resulting weight% of each of the major elements of the alloy were recorded. The accelerating voltages resulting in the closest weight% as determined by EDS to the ICP/AA analysis is presented in Table 2. Therefore, these accelerating voltages were used to characterize the composition of the alloy by EDS as a function of exposure time and location.

Table 2.
EDS Elemental Composition Determination of
7075-T6 Rod Stock Material for Specific Accelerating Voltages

Element	ICP/AA Avg Wt %	Acc Volt.	EDS Avg Wt %	Penetration depth (microns) ¹³
Al	90.09	30 keV	91.58	8.3
Cr	0.20	30 keV	0.12	3.4
Cu	1.31	5 keV	1.33	0.1
Mg	2.66	20 keV	2.86	6.3
Si	0.23	10 keV	0.33	1.5
Zn	5.49	10 keV	5.75	0.6

EDS Elemental Analysis – Field Exposed 7075-T6 Alloy Composition

Elemental analysis of the retrieved 7075-T6 epoxy mount samples from each of the three sites over 18 months were performed on corroded and non-corroded areas in the “as received” condition and after cleaning with DI water sonication.

Composition of Natural Seawater

The major components of natural seawater are listed in Table 3. The relative constancy of the ionic composition of seawater is well known.³² This constant relative composition has led to the definitions of chlorinity and salinity in standard oceanographic references.^{16,17} This constancy is evident in the similarity

in composition of the seawater sampled at NRL-KW and the composition of natural seawater reported in the literature.¹⁵ Therefore, the determination of the relative weight percents of chlorine (Cl), sodium (Na), sulfur (S), potassium (K) and calcium (Ca) by EDS on the 7075-T6 sample surfaces were investigated as indications of environmental deposition of some of the major component ions of seawater by air-sea interaction and transport on to the field exposed specimens.^{18,19} Due to magnesium being a component of the 7075-T6 alloy, and bromine *K* and *L* X-ray peaks overlapping with aluminum, these two elements were not included in the environmental determinations. Weight percent values of the environmental elements determined by EDS on the metal specimens were converted to PPM values to facilitate comparison to seawater composition measurements.²⁰

Table 3.
Major Components of Natural Seawater^{14,15}
At salinity of 35 ‰

Major Ions Of Seawater			
Ion	PPM (mg kg ⁻¹)	Wt%	% of Total Ions
Chloride	19344.000	1.934	55.275
Sodium	10780.000	1.078	30.803
Sulfate	2711.000	0.271	7.747
Magnesium	1283.000	0.128	3.666
Potassium	399.000	0.040	1.140
Calcium	411.900	0.041	1.177
Bromide	67.200	0.007	0.192
Total	34996.100	3.500	100.000

Table 4.
Major Components of Natural Seawater at NRL-KW²¹

NRL-KW Natural Seawater			
Ion	PPM (mg kg ⁻¹)	Wt%	% of Total Ions
Chloride	19825.740	1.983	55.671
Sodium	10820.050	1.082	30.383
Sulfate	2755.805	0.276	7.738
Magnesium	1363.675	0.136	3.829
Potassium	409.904	0.041	1.151
Calcium	353.748	0.035	0.993
Bromide	83.300	0.008	0.234
Total	35612.222	3.561	100.000

EDS Elemental Analysis – Field Exposed 7075-T6 Surface Environmental Composition

NRL-KW

Elemental analyses of the 7075-T6 specimens for environmental contaminants are presented in Figures 1 and 2. The average weight percent (wt.%) of the five elements are plotted as a function of the cumulative exposure time for pitted and non-pitted locations for each specimen. Comparing the results shown in Figures 1 and 2 it is clear that sodium is not present in either the pitted or non-pitted locations after DI cleaning; in addition, a decreasing trend in the remaining elements is evident for the pitted and non-pitted locations after DI cleaning, with sulfur having the higher wt.% of the five elements detected over the six quarters of exposure.