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Short communication

Chemical conditions inside occluded regions on corroding aircraft aluminum alloys

K.S. Lewis*, J. Yuan, R.G. Kelly

Center for Electrochemical Science and Engineering, Department of Materials, Science and Engineering, University of Virginia, Charlottesville, VA 22903, USA

Abstract

Corrosion of aluminum alloy structures costs the US Air Force in the order of US\$1×10⁹ annually. Corrosion develops in areas of overlap such as aircraft lap-splice joints and under protective organic coatings. Capillary electrophoresis (CE) has been used to determine the local chemistries at these corrosion sites of solutions that were extracted using a microsampling system. Analysis of the local solution within lap-splice joints from aircraft has been performed in two ways: rehydration of corrosion products and direct microsampling. The solutions collected were analyzed with CE to quantitatively determine the species present during corrosion. The most common ions detected were Cl⁻, NO₂⁻, NO₃⁻, HCO₃⁻, K⁺, Al³⁺, Ca²⁺, Na⁺ and Mg²⁺. Studies of the solution chemistry under local coating defects are required to understand coating failure and develop more durable coatings. A microsampling system and micro pH sensor were developed to extract solution from and measure pH in defects with diameters as small as 170 μm. Actively corroding defects contained high concentrations of Cl⁻, Al³⁺, Mg²⁺, Mn²⁺ and Cu²⁺ whereas only trace levels of Mg²⁺ were found in repassivated defects. The effects of these species on initiation and propagation of corrosion are discussed. © 1999 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

As the fleet of both civilian and military aircraft ages, the need for understanding the effects of corrosion becomes increasingly important. Every year, corrosion maintenance costs the United States Air Force approximately US\$1×10⁹. The KC-135 is an example of an aircraft that will soon exceed its original design life. Built in the mid-1950s, it is now expected to continue flying until the year 2040. Currently, there are over 600 KC135s still in service. In 1991, Groner determined that corrosion maintenance on KC-135s was costing US\$185 000 per aircraft per year [1]. Possible decreased mechanical strength due to corrosion, makes prevention, de-

tection and repair of corrosion not only a cost issue, but also a safety issue. Repair of corrosion can also detain an aircraft in a refurbishment center for an extended period of time leading to a lack of fleet readiness.

Two locations on aircraft where corrosion is prevalent are inside lap-splice joints and under organic coatings. Lap-splice joints consist of the region at which tow sheets of aircraft skin overlap and are riveted and/or spot welded together. Water and other species migrate into these joints by capillary action. In the past, these solutions have been assumed to be adequately modeled by 0.6 M sodium chloride, so this solution has been used for most mechanical testing of environmental effects on aircraft aluminum alloys. Organic coatings are used to protect aircraft from corrosion because they are easy

*Corresponding author.

to apply with low cost. Yet, solutions can diffuse through the coating carrying ionic species that can lead to corrosion at a defect. The goal of this work is to determine the actual solutions present within these joints and within blisters that form when corrosion occurs under organic coatings.

The application of capillary electrophoresis to the study of corrosion is relatively new. However, it is attractive because of the small volumes of solution found in corrosion sites. This work focuses on the retrieval and analysis of solutions less than 10 μl in volume. In addition CE is an excellent choice because of its sensitivity and ability to detect both anions and cations. It allows determination and quantitation of all of the soluble ionic species found in corroded regions with minimal solution preparation and overall ease of analysis.

2. Experimental

Two sampling methods were used to retrieve solution samples from lap-splice joints. The first method involved field sampling and was called the scraping method. While an aircraft was undergoing refurbishment at an Air Logistics Center (ALC), corrosion product was scraped off a newly opened joint. The scraping was performed using a rubber policeman placed on the end of a glass rod and the product was collected in a new Petri dish. The average mass of a scraping sample was 0.35 g. The soluble species were dissolved into solution by soaking the product in 2 ml of high-purity water for 24 h. That solution sample was separated into four vials for analysis by capillary electrophoresis. To date, 80 corrosion product samples from eight aircraft have been analyzed.

In order to obtain a sample from a joint in a laboratory setting, the microsampling method was used. A doubler (an extra sheet of aluminum added to an aircraft skin for additional strength) that was removed unopened and sent to the University of Virginia was opened. One panel was placed on one half of a 1.5"-diameter Petri dish which was filled with water (1"=2.54 cm). The panel and small Petri dish were then enclosed in a 3"-diameter Petri dish which was taped closed to maintain a high humidity

environment. After 24 h, solution was removed from the surface using a microsyringe controlled by a pump to extract accurate volumes. In preparation, the microsyringe was rinsed with high-purity water and then 1 μl of mineral oil was drawn into the syringe to create a barrier and prevent dilution of the sample. Using an optical microscope at magnification 10 \times , the tip of the syringe was placed on the wetted corrosion product. The solution was removed and then expelled into the lid of a capillary electrophoresis vial. A known amount of water (20–50 μl) was then added and the sample transferred into the bottom of the vial.

The microsampling method was also used to retrieve solution samples from within blisters on organic coatings. A vinyl coating was applied using spin coating to a panel of aluminum alloy 2024-T3, an alloy commonly used in aircraft structures. The thickness of the coating was approximately 10 μm . The coated panel was then exposed to either 0.6 M NaCl or 0.1 M KCl for 14–18 days. This soak time caused blisters to form at a limited number of discrete sites in the coated system. To remove the solution from the blisters, the tip of the microsyringe was inserted through the coating. Solution volumes from 0.4 to 10 μl were extracted and transferred to CE vials using any necessary dilution. Historically, only solutions from blisters with greater than 10 mm diameter could be analyzed [2], but this technique allowed analysis of blisters as small as 1 mm in diameter.

Solution analyses were performed using a capillary electrophoresis system. Four electrolytes were used to analyze each sample. Chromate and phosphate were used to analyze for anions and UVCat1™ and UVCat2™ were used for cations. This approach allowed for comparison between methods and the ability to analyze for ions that are detected in only one electrolyte. For example, aluminum can only be detected using a modified UVCat2™. Each electrolyte had dedicated plasticware and capillaries. Run times varied with electrolytes because of differing migration times in the different matrices (6 min for chromate and phosphate, 8 min for UVCat2™, and 12 min for UVCat1™). Components were identified by matching their migration time with the migration time of known species and/or sample spiking. Quantification was performed by comparison of

Table 1
Comparisons of concentration ratios in scraping and microsampling methods

	Microsample	Scraping	Factor difference
Nitrate:chloride	0.18	0.25	1.4
Nitrite:chloride	0.05	0.07	1.4
Potassium:sodium	14.20	17.75	1.3
Magnesium:sodium	29.40	33.31	1.1
Aluminum:sodium	6.10	54.44	8.9

time-corrected peak areas to calibration curves generated from standards of known concentrations.

3. Results

To examine the effectiveness of microsampling, the scraping and microsampling methods were used on the same piece of a doubler in the laboratory. Scrapings were taken first and then the doubler was exposed to the high-humidity environment for 24 h before microsampling. Both solution samples were run in the same carousel in the CE to eliminate any effects caused by differences in migration time that may occur from day to day. Three samples were taken by each method. The same ions were detected for each pair. While it is known that the microsamples were diluted 1:6 as they were transferred to the

CE vial, the dilution of the scraping samples is unknown. Because of this, the concentrations are presented in ratios to eliminate the effects of dilution. As shown in Table 1, the ratios are within a factor of two for all ions except aluminum. The ratio of aluminum to sodium is typically at least four times greater in samples obtained by the scraping method than those from the microsampling method. This result is likely due to excessive pressure applied to remove corrosion product causing some of the underlying metal to be removed as well or the need for more water in the microsampling method to dissolve all of the aluminum ion in the corrosion product.

The common anions found in the solutions derived from corrosion product found in aircraft lap-splice joints were chloride, sulfate, nitrate and hydrogen carbonate. Aluminum potassium, sodium and magnesium were common cations. Common ions are those that are present in at least 75% of the sample solutions. Sample electropherograms showing the common ions detected are shown in Fig. 1. Also detected in at least three samples were nitrite, fluoride, phosphate, acetate, chloroacetate, propionate, formate, lactate, oxalate, phthalate, butyrate, calcium, manganese, zinc, strontium, lithium, barium and copper for a total of 26 different ions.

The ions detected in the samples varied greatly. No sample analyzed to date has contained all 26 of the ions that have been detected. Table 2(a) shows

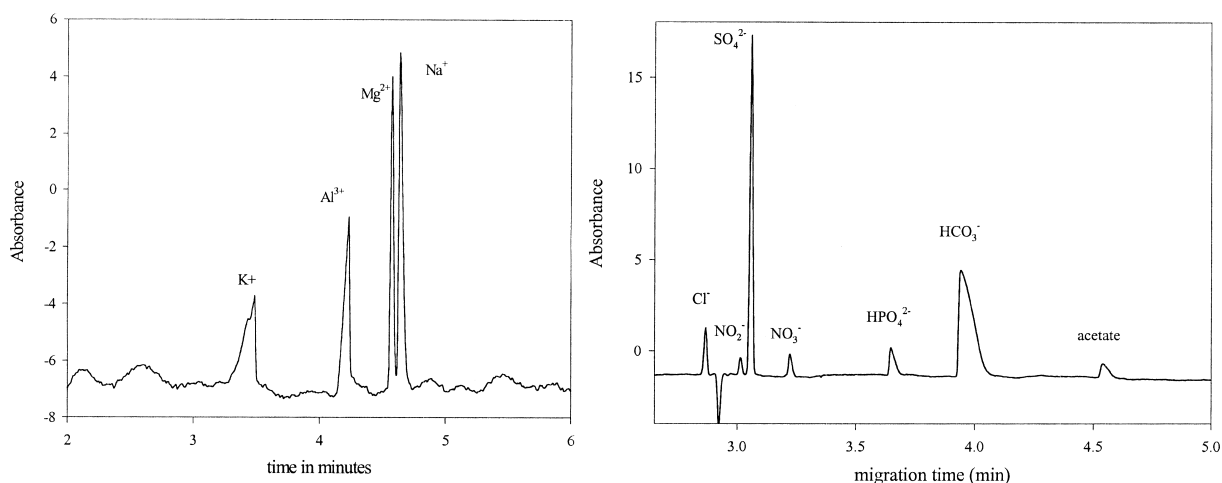


Fig. 1. Sample electropherograms showing common ions detected in lap-splice joints.

Table 2
Variability of lap-splice joint samples in: (a) anions detected; and (b) concentration of chloride measured

(a) Anions detected			
Ion	% Samples containing ion	Ion	% Samples containing ion
Chloride	78	Nitrite	63
Nitrate	94	Sulfate	87
Fluoride	32	Phosphate	46
Hydrogen carbonate	83	Acetate	79
Chloroacetate	6	Propionate	47
Butyrate	35		

(b) Conc. of chloride measured			
Conc. of Cl (mM)	No. of samples with conc. of Cl	Conc. of Cl (mM)	No. of samples with conc. of Cl
0	14	0.50–1.00	4
<0.01	6	1.00–5.00	6
0.01–0.05	12	5.00–10.00	0
0.10–0.50	13	>10.00	6

the percentage of samples that contained each anion. While variability from one aircraft to another is expected because of different environments to which different aircraft are exposed, significant variability within a set of samples from the same aircraft was also found. Along with the variability in ions detected, there was also a large range of concentrations detected, as shown in Table 2(b). The variation in ions and concentrations makes determination of a solution with exact concentrations found within all aircraft lap-splice joints impossible. However, a solution with the same electrochemical behavior can be derived. It is important to note that the sum of all the highest measured concentrations for each ion is less than 80 mM. By statistical examination of electrochemical tests, the important parameters in determination of corrosion rate, potential and morphology were determined [3]. The final solution developed from that testing contains 20 mM chloride, 4 mM nitrite, 4 mM hydrogen carbonate, and 2 mM fluoride at pH 9.

Exposure of the coated samples to the salt solutions led to the development of small blisters (1–7 mm diameter). Fig. 2 demonstrates that there is sufficient sensitivity with CE to analyze solutions from very small blisters (1.5 mm, 100 nl, with subsequent dilution by 100×). The cations detected had their origin in the bulk solution (Na^+) and from

the dissolution of the alloy substrate (Mg^{2+} , Cu^{2+} and Zn^{2+}). A separate analysis was performed for Al^{3+} [4,5]. Anions observed include Cl^- (from the bulk solution) as well as small organic acids (formate, acetate) which appear to originate from degradation of the organic coating within the blister

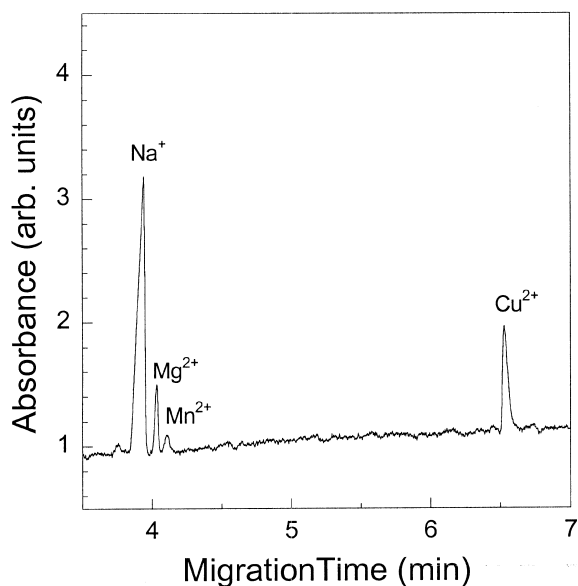


Fig. 2. Cation analysis of solution retrieved from within a 1.5 mm blister.

solution. Calculations based on the concentrations observed and the known dilutions used showed that a minimum blister size of 500 μm diameter could have its solutions analyzed with CE. These calculations demonstrate that increased sensitivity of the analysis method is not needed as much as an increase in the ability to find and consistently sample from blisters of this size. Sampling from the blisters can be complicated by the presence of corrosion products within the blister and their flattened (non-hemispherical) shape.

Similar studies in KCl solutions yielded similar corrosion results, but allowed more accurate quantitation because of the increased separation between K^+ and the other cations in electropherograms. Actively growing blisters were found to contain a solution concentrated in the alloy constituents and Cl^- . The highest concentrations of the organic acids were also found in these blisters. These active blisters also appeared red in color due to the presence of metallic copper on the surface. In some cases, active blisters ceased growing and turned black in appearance. These blisters contained much lower concentrations of all ions. Clear blisters have also been observed in which very little corrosion occurs, but a delamination of the coating from the substrate is detectable. Generally, red and black blisters had lower K^+ concentrations than the bulk environment, whereas clear blisters had higher K^+ concentrations. Red blisters also had substantially increased chloride concentrations relative to the bulk. These blisters have very low concentrations of alloy ions. Measurements of pH within the blisters [4] showed that the red blisters had pH values in the range 3–4, the black blisters had pH values in the range 5–6, and the clear blisters had pH values of 8.5–9.5.

4. Discussion

The microsampling technique has been shown to be an accurate method for obtaining samples from occluded regions on aging aircraft. The small volumes of solution that are present in these regions require a retrieval technique that can obtain these small volumes with minimal contamination. The microsampling technique is capable of retrieving

volumes as small as tens of nl. These samples can be diluted with known amounts of water to volumes that can be analyzed with capillary electrophoresis. The concentrations found within these occluded regions can be detected in CE analysis with the necessary dilution.

The CE analysis determined that there are many ions present within aircraft lap-splice joints. This result questions the applicability of corrosion and mechanical testing performed in 0.6 *M* sodium chloride solution as it is not the standard environment present within these joints. The chemical environment is complex as all samples contained at least eight of the detected ions. The solution is also dilute with a total ionic concentration of less than 80 mM. The solution that was developed from capillary electrophoresis results and statistical analysis of electrochemical tests is a more accurate environment for future corrosion and mechanical tests.

The results from the coating defect study are consistent with the current state of understanding of occluded chemistry in corroding Al alloys [6], but represent one of the very few quantitative analyses of such environments [7]. The red blisters represent sites of localized dissolution, with the majority of the cathodic reaction occurring elsewhere. The formation of metallic copper on the alloy surface within the blister is the result of either a dissolution–redeposition process, or surface diffusion of copper left behind by dissolution of the other alloy components. The accumulation of higher concentrations of chloride results from the need to maintain electroneutrality within the blister solution. The creation of cations (by alloy dissolution) leads to an electrostatic driving force for anions through the coating. The clear blisters are likely the location of the cathodic reactions that support the actively growing blisters. Both of the common cathodic reactions in aqueous corrosion (oxygen and water reduction) lead to an increase in the local pH, and would tend to concentrate cations from the bulk environment to maintain electroneutrality. The case of the black blisters is interesting in that it should represent an intermediate case. Unfortunately, there are insufficient data to date to make conclusions.

The attack of the organic coating itself by solutions formed in blisters leads to the detection of small organic acids. Such acids are also seen in the

clear high-pH blisters, indicating that both acid and alkaline hydrolysis of these coatings is possible. The results are an example of the strength and importance of CE as a screening tool in corrosion solution analysis. Its ability to efficiently detect a wide variety of species diminishes the likelihood of overlooking an important species. The organic acid results will also assist in the determination of the contributions of various mechanisms by which blisters in organic coatings on metals grow. If the interface between the coating and the metal is susceptible to attack on the coating side, then organic acids will be produced. Undercutting of the coating by dissolution of the metal can also occur. Determination of the relative contributions of these paths will be part of future work in this area in order to provide information for the design of better protective coating systems.

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