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Chromatographic studies of corrosion sites in metallic materials

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ABSTRACT

Many types of corrosion phenomena are controlled by the ionic composition of a small volume of solution at the surface. Localized corrosion and atmospheric corrosion are two examples in which < 1 μl of solution can cause dramatic damage. Ion chromatographic (IC) techniques have been used to analyze these solutions in order to gain a better understanding of the mechanisms which govern them. Two examples are presented. The presence of minor alloying elements at localized corrosion sites in two aluminum alloys has been demonstrated, indicating non-stoichiometric dissolution of the alloy during localized corrosion. In addition, IC analysis allowed the determination of the species responsible for the atmospheric corrosion failure of electrical connectors, including their likely origin.

INTRODUCTION

The corrosion of metals is intimately tied to the composition of the solution layer next to the material surface. This solution not only affects the metal dissolution rate and mechanism, but the solution composition is also affected by the chemical and electrochemical processes involved with metal dissolution. In cases where there is restricted mass transport, the composition of the solution adjacent to the metal surface can change dramatically [1–3]. Two corrosion phenomena in which severe mass transport restrictions normally occur are localized corrosion and atmospheric corrosion. Both of these types of corrosion are inherently difficult to study due to the small volumes of solution associated with the corrosive action. In both cases, typically volumes of < 1 μl contain the species of interest. In most cases, the elemental composition of the solution is of limited use; it is the ionic composition that determines the nature and severity of the corrosion that occurs. Recently, the utility of ion chromatography (IC) to the study of corrosion problems was demonstrated [4–6]. In this paper, after giving background information on the two types of corrosion phenomena, the application of IC to the localized corrosion of aluminum alloys and to the failure analysis of electrical components which had undergone atmospheric corrosion is presented.

Localized corrosion

Localized corrosion describes attack that occurs at discrete sites on a material surface rather than uniformly over the entire surface. If often occurs at physical or chemical inhomogeneities on the surface. Such inhomogeneities can result from (a) deposits that develop during service, (b) areas enclosed between two materials (crevices), or (c) the formation of additional phases in the alloy. During the propagation of this attack, the chemical composition of the surface site and/or local solution volume is altered due a combination of the restricted mass transport and hydrolysis reactions of the dissolution products [1–3]. This altered solution is much more aggressive than the bulk solution, leading to accelerated, localized attack. The mechanism(s) which lead to this behavior are still the sub-

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ject of debate [7–9]. Unfortunately, due to the limited volumes of solution in such localized sites (typically < 1 μl), little detail is known about their composition or the effects of important experimental variables such as alloy composition and electrochemical potential. These and other variables can have large effects on the observed localized corrosion behavior. Thus, in order to test present models rigorously and develop more accurate ones, a better understanding of the chemical composition of these sites is required.

Failure analysis of meter socket

Atmospheric corrosion can lead to the failure of electronic components. This type of attack takes place in electrolyte layers that are between 10 monolayers and 10 μm thick which form on surfaces due to the dissolution of pollutant gases into the adsorbed water layers present under ambient conditions (near room temperature, relative humidity above 60%). The absolute rates of attack can be small, but due to the low corrosion tolerances allowed for electrical connectors, even low rates are unacceptable if they produce resistive films. Often, traditional post-exposure analysis of failed components does not reveal the nature or origin of the aggressive specie(s). In such cases, it is difficult to prevent future failures.

One example of such a case follows. In 1989, a production run of galvanized steel meter sockets (galvanized steel cases used to encase household electric or gas meters) were manufactured and packaged along with their fastener kits in cardboard boxes before being inventoried in a warehouse. In 1992, severe corrosive attack of a number of the sockets was discovered. The following observations were made:

(1) Attack was not a function of storage location either within the storehouse or within a given pallet of packaged meter sockets.

(2) Attack occurred on the exterior and interior of socket casings, as well as within polymer bags containing fasteners, and thus did not require direct contact with the cardboard packing material.

(3) Galvanized steel components were especially attacked producing red rust and a white (presumably zinc-containing) corrosion product.

(4) The problem was not typical and appeared to be limited to a single manufacturing lot.

While the portion of the surfaces exposed to the air space showed attack, those portions of the surfaces in contact with each other were not attacked. The consistent observation of such a corrosion morphology indicates that the corrosion did not occur due to condensation of a large water layer. These facts implied that the corrosive agent was in the vapor form and was especially aggressive towards iron and zinc. In addition, only some packages contained sockets that were attacked. However, inside a package that contained corroded components, all components were attacked, including parts enclosed in (unsealed) plastic bags. Identification of the specie(s) responsible for the attack, as well as their origin, was required in order to prevent future failures.

This paper will discuss the application of IC to studies of localized corrosion as well as vapor-phase corrosion. In both cases, the technique's mass sensitivity, ability to ionically speciate and ability to use small injection volumes were critical to developing a better understanding of these processes.

EXPERIMENTAL

Localized corrosion testing

Two commercial aluminum alloys were studied. Alloy 2024 contains 4.4% (w/w) Cu, 0.6% (w/w) Mn, and 1.5% (w/w) Mg. Alloy 8090 contains 2.4% (w/w) Li, 1.2% (w/w) Cu, 0.7% (w/w) Mg and 0.12% (w/w) Zr. Both are important materials in the aerospace industry due to their low density and excellent mechanical properties. Crevices were formed by clamping an alloy specimen between two cylinders of PTFE (1 cm diameter) via the device shown in Fig. 1. This simulates the type of crevice corrosion testing used [10], as well as the crevice formed by a gasket, for example. The electrical connection to the specimen was insulated from the solution. This arrangement allowed the application of a known torque of 0.23 Nm. This pressure corresponded to a total crevice volume of 2.4 μl. This volume was checked by placing 1.2 μl of water onto one side of the alloy surface and pressing PTFE crevice former onto the surface with 0.23 Nm torque. The 1.2 μl just covered the surface to the edge of the crevice former. A Princeton Applied Research Model 173 Potentiostat was used to apply a set potential between the aluminum alloy surface

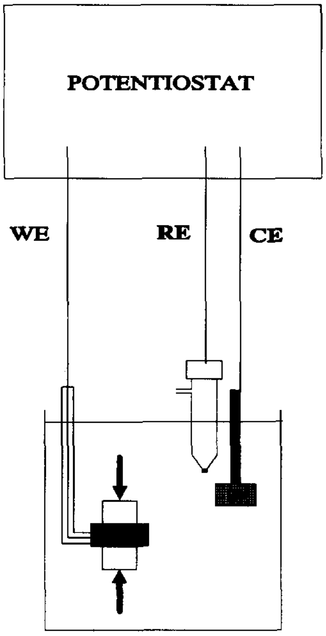

Fig. 1. Experimental schematic of crevice former. The potentiostat is used to control the potential between the working electrode (WE) (aluminum alloy specimen) and the reference electrode (RE). The PTFE crevice formers are clamped to the surface with a variable pressure apparatus (not shown). CE = Counter electrode.

and a saturated calomel (SCE) reference electrode in a test solution of 0.35% (w/w) KCl. A platinized niobium counter electrode was also connected to the potentiostat, and the apparatus was placed in a vessel containing the test solution. The potential of the sample was then scanned at 0.5 mV/s first in the anodic direction from 100 mV below the specimen's corrosion potential to a potential at which the applied current was 1 mA/cm^2. The direction of the scan was then reversed and the potential was scanned in the cathodic direction until the intial potential was reached. All potentials cited are *versus* SCE. After the scan complete, the clamped sample was removed from the solution, the clamp carefully loosened, and the sample as well as the crevice formers were soaked in 5 ml of 18 MΩ cm water in a PTFE beaker. A sample of this solution was then analyzed chromatographically.

Atmospheric corrosion

A similar approach was used for the meter socket analysis. Samples of both corroded and uncorroded components were selected. In order to investigate the source of species found, samples of cardboard packaging material were cut from the accompanying boxes. In each case, the samples were immersed and soaked for 45 min in approximately 10 ml of 18 MΩ cm water from a Barnstead purification unit. Samples of each solution were analyzed chromatographically.

Chromatography

For all experiments, a Waters Action Analyzer and a Rheodyne injector with a 100-μl fixed loop were used. For the localized corrosion experiments, the dissolution of the minor alkali and alkali earth elements was of interst. A Waters Mono-di column (150 mm × 3.9 mm I.D.) was used. The eluent consisted of 3 m*M* HNO_3 with 0.1 m*M* EDTA [11]. The flow-rate was 1 ml/min, and indirect conductivity detection was accomplished via a Waters Model 431 conductivity detector. The eluent for this method has a high background conductivity (1150 μS) and thus indirect conductivity was used. In such detection, a decrease in the conductivity of the solution passing through the detector (*e.g.*, due to the passage of the void volume) will be observed as a positive peak in the chromatogram. Standards were made from reagent grade salts, except for Al^{3+} which was made from a 1000 mg/l atomic absorption standard. All water used was 18 MΩ cm from a Barnstead purification unit.

For the atmospheric corrosion work, inorganic acid anions were separated and analyzed with a Waters IC Pak-A column and a borate–gluconate eluent. Organic acid anions were separated and analyzed with a Waters ion exclusion column (300 mm × 7.8 mm I.D.) and an octane sulfonic acid eluent [12]. In both cases, conductivity detection with a Model 431 conductivity detector was used.

RESULTS

Localized corrosion

Fig. 2 shows the chromatogram obtained when a mixture of Li^+, Al^{3+}, K^+, and Mg^{2+} is injected. The dip in the chromatogram following the Li^+ is due to the presence of the Al^{3+} as discussed below.

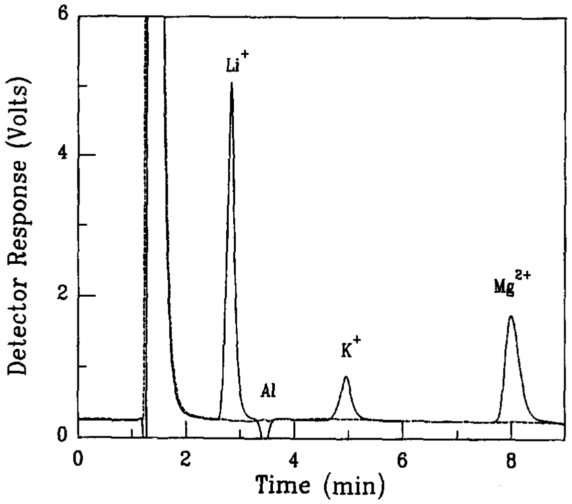

Fig. 2. Chromatogram of standard containing Li^+, K^+, Mg^{2+} and Al^{3+} using indirect conductivity detection. Also included is a water injection. The presence of aluminum does not compromise the analysis of the other components. ——— = Standard; --- = water.

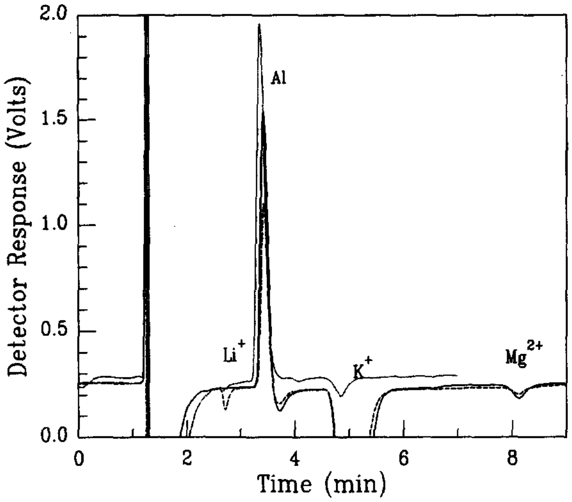

Fig. 4. Chromatogram of solutions from Fig. 3 using direct conductivity detection. The alkali and alkali earth metals now appear as negative peaks, while the presence of aluminum causes a positive peak to appear. ——— = Alloy 2024; --- = alloy 8090; ····· = 5 ppm standard.

An injection of pure water is included for comparison. Note the small Na^+ peak at $t = 3.4$ min. Fig. 3 shows the chromatograms resulting from the injection of the rinse solutions from the crevice sites of the two alloys, as well as from an injection of the deionized water. The detection of the minor alloying elements (Li and Mg) from the two alloys is clear. The large K^+ peak is due to the KCl used in the test solution. Fig. 4 shows chromatograms resulting from injections of the same solutions as used in Fig. 3 as well as the Al^{3+}-containing standard of Fig. 2, but with direct, rather than indirect, conductivity detection. It appears that the presence of Al^{3+} in the sample causes a positive peak during direct detection. It elutes at the same time as Na^+, but with the opposite effect on conductivity. Determination of the origin of this peak is presently underway.

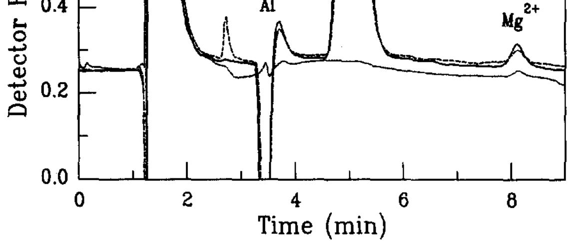

Fig. 3. Chromatogram of solutions extracted from aluminum alloy crevices. In both cases, Mg is detected, while from the Alloy 8090 crevice, Li^+ is detected as well. Also included is a water injection. ——— = Alloy 2024; --- = aloy 8090; ····· = water blank.

Failure of meter socket

In order to determine the cause of the failure, a series of analyses were performed, including analysis for organic acids. Fig. 5 shows two chromatograms from the organic acid analyses: the rinse solution from an attacked bolt; and the rinse solution from an identical, but unattacked, bolt. The presence of large amounts of formate and acetate on the attacked bolt and their absence on the unattacked bolt is clearly shown. Fig. 6 shows an overlay of two chromatograms: the soak solution from a piece of

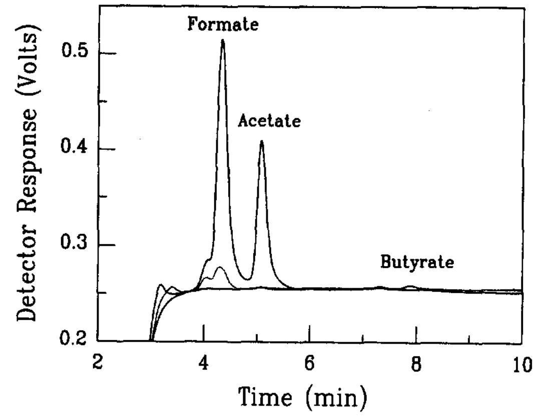

Fig. 5. Chromatogram of rinse solutions from a corroded component (———), and an uncorroded component (····). Also included is a water injection.

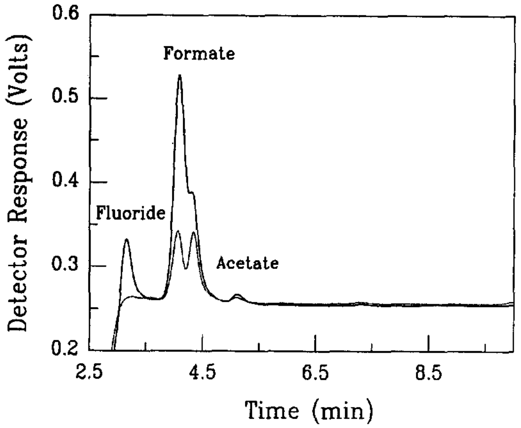

Fig. 6. Chromatogram of soak solutions from cardboard packaging material that contained corroded components (———), and uncorroded components (····).

the cardboard packaging that contained attacked components; and the soak solution from an identical piece of the cardboard packaging that contained unattacked components. The correlation between the presence of organic acids and corrosive attack is maintained.

DISCUSSION

Localized corrosion

Recently, the use of IC for the speciation of the chemical composition of solutions extracted from localized corrosion sites in stainless steel was demonstrated [4–6]. The present work extends that approach to another alloy system, precipitation hardened aluminum alloys. Aluminum alloys are fairly dilute with the sum of all alloying elements comprising approximately 10% (w/w) of the alloy. These alloying elements provide the means by which aluminum alloys are made technologically useful by increasing both the material's strength and stiffness [13,14]. However, they also decrease the localized corrosion resistance [14], though the operational mechanisms are uncertain. The present work demonstrates that IC is capable of detecting the minor alloying elements even in the presence of large amounts of Al^{3+}. Clearly, the minor alloying elements are preferentially dissolving, though quantitation of the degree of non-stoichiometric dissolution remains to be done. In addition, the presence of the Al^{3+} leads to a peak coincident with Na^+, but with an opposite polarity. Present work is aimed at determining the correspondence of this peak with the presence of an aluminum specie.

Failure of meter socket

The results of the IC analysis of the rinse/soak solutions from the meter socket bolts provided the critical information necessary to determine: (a) the cause of failure, (b) the identity of the aggressive species as well as (c) the source of the aggressive species. Both iron and zinc are quite susceptible to vapor-phase attack by organic acids [15]. The comparative IC analysis demonstrates that such attack took place inside the packages in which corroded components were found (Fig. 5). Conventional analyses of the corrosion products using X-ray diffraction and energy dispersive spectroscopy revealed little except for the presence of a sodium zinc sulfite on some corroded parts. The most likely source of the organic acids is the cardboard packaging material (Fig. 6). One possible scenario as to the origin and progression of the corrosion is as follows. Incomplete washing of the pulp used to make the cardboard allowed retention of organic acids (and inorganic ions such as sulfite) in the finished product. During the long (3 years) storage time, some of the acids vaporized and attacked the metallic surfaces. Further investigation revealed that all of the attacked components were packaged in cardboard manufactured in a single lot, while the unattacked sockets were packaged in cardboard manufactured in a different lot. This lends additional credence to the suspected source of the aggressive species.

This example clearly shows the utility of IC for corrosion failure analysis. Its ability to ionically speciate small volumes of solution with high mass sensitivity makes it especially attractive for corrosion analyses in which small volumes of solution at the metal/solution interface often control the nature and rate of the important processes.

At the present time, the application of capillary electrophoresis is also being pursued as a tool for corrosion failure analysis as well as both applied and fundamental studies of corrosion phenomena. With its combination of excellent detection limits and very small sample solution volumes required, capillary electrophoresis appears to be an ideal technique for such work.

ACKNOWLEDGEMENTS

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