

Application of ion chromatography to corrosion studies

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ABSTRACT

The corrosion of metals is controlled by the chemical composition of the solution at the metal surface. During localized corrosion, the composition of the solution close to the metal/solution interface can become very different from the bulk solution composition due to the occurrence of electrochemical and chemical reactions at the surface. Considering the controlling influence of this solution, determining its composition would be indispensable for improving the understanding of metallic corrosion. Analysis of the transition metal dissolution products of stainless steel under uniform corrosion, pitting corrosion and crevice corrosion conditions has been accomplished.

INTRODUCTION

The corrosion of metals is controlled by the chemical composition of the solution at the metal surface. This solution can often have a radically different composition from that of the bulk. Such a situation can develop on metal surfaces due to restricted mass transport and its coupling to the electrochemical and chemical reactions which cause corrosion. One example where this is of importance is localized corrosion.

Localized corrosion of metals and alloys in aqueous environments is an especially damaging form of environmental attack due to its unpredictability, the difficulties involved in its detection, and the limited efficacy of mitigation strategies. Since localized corrosion is the major corrosion problem for many highly alloyed materials, efforts aimed at understanding its various forms have been the focus of much attention. It has become generally accepted that the cause of the propagation of localized corrosion sites (*e.g.*, pits, crevices, cracks) is the development of an highly aggressive environment in the occluded cell which comprises the area of attack. While there have been recent advances in the modelling and simulation of such environments, the measurement of the development of the chemistry

of these sites has not been possible. Hence, the observed improvement of the localized corrosion resistance of stainless steels with the addition of various alloying elements (such as nitrogen and molybdenum) and solution inhibitors (such as sulfate and nitrate) has remained unexplained.

While there are a variety of types of localized corrosion phenomena (*e.g.*, crevice corrosion, pitting, intergranular attack, stress-corrosion cracking) they share a number of commonalities. Foremost among these is the development of an extremely aggressive solution locally which causes high rate, localized attack. It is becoming increasingly clear that much can be understood about the different types of localized corrosion by considering them different manifestations of the same basic phenomena [1–3]. For example, pitting can be viewed as crevice corrosion on a smaller scale, with either micropores or surface heterogeneities acting to form the crevice. The controlling factor in localized corrosion is the development and maintenance of the aggressive chemistry at the local site. Despite its importance, little is known about this chemistry.

Crevice corrosion occurs on a metal or alloy at locations where the bulk solution has restricted access. This can occur at the meeting points of flanges and gaskets. The rate of attack inside the crevice

formed by the gasket can be orders of magnitude higher than the rate on the surfaces that are boldly exposed to the bulk electrolyte. In order to understand this type of attack, a better insight into the chemistry of the localized site and how it changes with time is required. However, the sampling of the most important solution is the most difficult due to the restricted geometry. By their very nature, crevices contain small volumes of electrolyte. Past work [1,3] has preliminarily characterized the solution chemistry for an established localized corrosion site in stainless steels as a low pH, concentrated metal chloride solution. However, a great deal of important information concerning the solution is missing. For example, the presence and concentration of the various alloying elements in the localized corrosion site is not well characterized. In addition, the valence of some species in these solutions is also uncertain. The excellent mass sensitivity of ion chromatography, along with its ability to speciate the ionic state of the elements, makes it extremely attractive for studying the localized corrosion behavior of metals and alloys. Its ability to handle small injection volumes also makes it amenable to cases of analysis of the small volumes associated with localized corrosion.

This paper reports the initial results of the application of ion chromatography (IC) to the localized corrosion of stainless steels. The effects of solution and alloy composition as well as potential on the transition metal content of artificial pits are shown. In addition, the extraction and analysis of extremely small volumes of solution from a real crevice formed by pressing a deformable material onto stainless steel is demonstrated.

EXPERIMENTAL

Electrochemical testing

Fig. 1 shows a schematic of the experimental arrangement. A 6-mm diameter rod of stainless steel (SS, Type 304 or 316) was mounted in a room temperature curing epoxy. Electrical connection was made to the specimen via a previously spot-welded wire. The surface was ground flat and polished with silicon carbide paper of successively finer grit size, ending with 600 grit. An artificial pit was formed by placing another cylinder of the epoxy, with a 6-mm hole drilled through it, on top of the mounted stain-

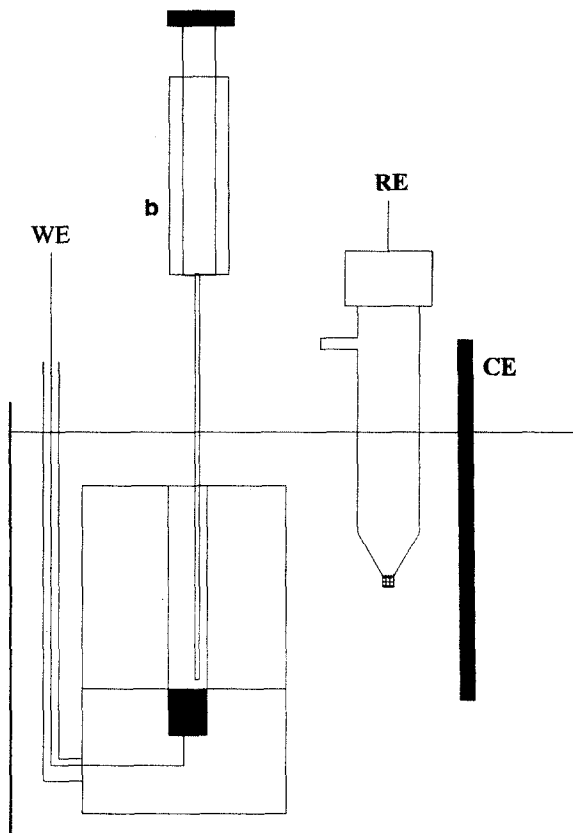


Fig. 1. Schematic of artificial pit apparatus. WE = Working electrode connection to voltage control device (potentiostat). The stainless-steel specimens were the working electrodes. RE = Reference electrode connection to potentiostat. A saturated calomel electrode was used. CE = Counter electrode connection to potentiostat. A graphite rod was used. b = 1-ml syringe used to withdraw solution from artificial pit cavity. Clamping device used to hold artificial pit together not shown.

less steel so that the hole was concurrent with the specimen surface. The upper cylinder was held in place via a clamping device. The entire artificial pit was then placed in a beaker containing the test solution (either 1 M hydrochloric acid or 1000 mg/l hydrochloric acid + 1000 mg/l sodium chloride). This "lead in pencil" arrangement insures that the dissolution products which form during the test remain in the artificial pit cavity due to the restricted diffusion. A more detailed description of the artificial pit method can be found elsewhere [4]. The length of the upper cylinder (25 mm) as compared to the electrode diameter leads to an estimate of 100

h for the diffusion time, if one dimensional diffusion is assumed to occur. No test reported here lasted longer than 2 h.

A saturated calomel (SCE) reference electrode and a graphite rod to be used as a counter electrode were also placed in the beaker as shown in Fig. 1. The beaker was open to air. A Princeton Applied Research Model 173 Potentiostat with a Model 276 Computer Interface applied a set potential between the working electrode (the stainless steel) and the reference electrode. All potentials are quoted *versus* SCE. A typical experiment consisted of first immersing the artificial pit and polarizing it to a set potential for a set period of time. During this time, the current necessary to maintain the potential was recorded. At the end of the set time, a 1-ml syringe was used to remove 700 μl of the artificial pit solution. This sample was placed in a 1-ml vial. It was diluted as necessary with 18 M Ω cm water from a Barnstead purification system.

Chromatography

For all experiments, a Waters Action Analyzer was used. The system is equipped with a Model 486 tunable absorbance detector, along with a reagent delivery module. A Rheodyne injector was used with a 100- μl fixed loop. For the analysis of transition metals, a gradient method was developed to allow for the simultaneous determination of Fe^{3+} , Cr^{3+} , Cu^{2+} , Pb^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} , Fe^{2+} and Mn^{2+} . This method is a gradient adaptation of a method developed for transition metals by Cassidy and Elchuk [5] in which separation occurs on a C_{18} column that is dynamically coated with sodium octanesulfonate. The initial eluent is a pH 3.4, 20 mM tartrate buffer, with 2 mM sodium octanesulfonate and 5% acetonitrile. After 4.5 min at 0.8 ml/min isocratically, the tartrate concentration is increased parabolically to 35 mM over the next 15.5 min as shown in Fig. 2. During this time the other conditions (pH, flow-rate, octanesulfonate and acetonitrile concentrations) are kept constant. Post-column derivatization was done with PAR [0.2 mM 4-(2-pyridylazo)resorcinol, 3 M NH_4OH , 1 M acetic acid]. It was combined with the eluent via nitrogen gas pressure at 0.5 ml/min. The resulting metal ion-PAR complex was detected by measuring the absorbance at 500 nm.

Calibration curves were generated which includ-

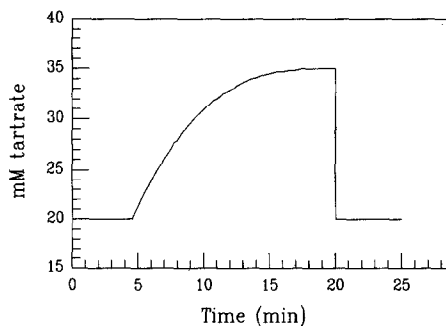


Fig. 2. Tartrate gradient profile used for the transition metal analysis. The concentrations of the other constituents were held constant throughout the analysis: pH 3.4, 2 mM sodium octanesulfonate and 5% acetonitrile. The eluent flow-rate was 0.8 ml/min, and the post-column reagent flow-rate was 0.5 ml/min.

ed within their range the concentrations expected in the test solutions. All calibration curves showed excellent linearity, with correlation coefficients of greater than 0.995 for concentration ranges from 0.01 to 2 ppm for all ions for which analyses were made. Further details of the development and statistical analysis of the method will appear elsewhere [6].

RESULTS AND DISCUSSION

Fig. 3 shows the chromatogram of a standard solution consisting of 1 mg/l of each of the metals indicated in the figure. Related work [7] has shown that the sensitivity of this approach allows 10 $\mu\text{g/l}$ or less of each metal to be detected. It is clear from

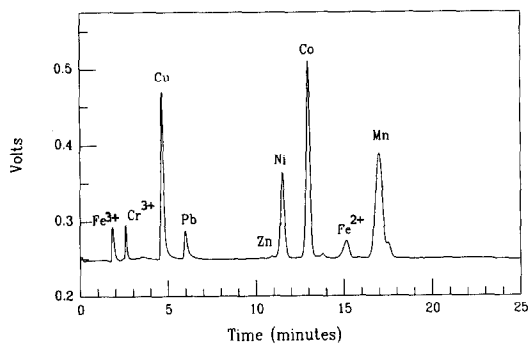


Fig. 3. Chromatogram of 1 ppm each of the transition metals labeled. The voltage cited is the output of the absorbance detector. The standard was made in high purity water from atomic absorption standards. The small Zn peak is an impurity.

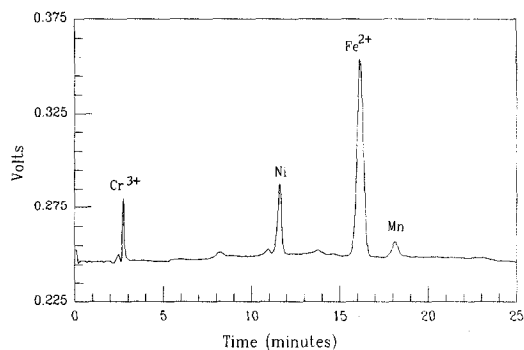


Fig. 4. Chromatogram of solution removed from artificial pit apparatus with 304 SS in 1 M hydrochloric acid, -0.1 V (SCE).

this figure that detection of the different transition metals in solution is straightforward. For iron, it is also possible to discriminate between the ferrous and ferric states.

Since it is generally accepted that the environments within localized corrosion sites of stainless steel have low pH and a high $[\text{Cl}^-]$, some occluded cell experiments were performed in 1 M hydrochloric acid. The chromatogram which results from analysis of the solution extracted from an artificial pit of 304 SS held at -0.1 V (SCE) is shown in Fig. 4. An analysis of the relative abundance of the different metals in the extracted pit solutions is shown in Table I, along with the results for 304 SS held at a higher potential. It is immediately clear that Cr is underrepresented in the solution compared to its concentration in the alloy (18%), while Ni (10% in alloy) and Mn ($< 2\%$ in alloy) have been preferentially dissolved.

The results of potentiostatically holding 304 SS at $+0.7$ V (SCE) for 30 min in a less aggressive solu-

tion (1000 mg/l sodium chloride + 1000 mg/l hydrochloric acid) on the solution composition within the artificial pit are shown in Fig. 5. Pitting, rather than uniform dissolution, occurs under these conditions. The large amount of manganese relative to its concentration in the base alloy again indicates preferential dissolution of Mn (most likely from MnS inclusions), while again Cr^{3+} is underrepresented when compared to its concentration in the alloy. It should be noted that under these conditions (a higher pH compared to the 1 M hydrochloric acid), some Cr may have dissolved but precipitated as chromium oxide, and would therefore not be detected. The origin of Fe^{3+} is most likely the oxidation of the Fe^{2+} by dissolved oxygen. Changes in the experimental apparatus to allow for deaeration are planned. The splitting of the Fe^{2+} peak only occurs when there is a high concentration of Cl^- in the injected sample and may be due to the presence of a ferrous chloride complex. This would be analogous to the aluminum fluoride complexes previously detected chromatographically [8].

A 304 SS sample was partially covered with a piece of PTFE to form a crevice through the application of pressure from the clamping device. This simulates the type of crevice corrosion testing used [9], as well as the crevice formed by a gasket, for example. It was also felt to provide a challenging test for the experimental approach, as the crevice volume in this case would be well less than $1 \mu\text{l}$. The sample was then polarized to $+0.2$ V (SCE) where crevice corrosion initiated almost immediately. After 3700 s, the sample was removed from the solution, the clamp carefully loosened and the two faces of the crevice rinsed with $300 \mu\text{l}$ of $18 \text{ M}\Omega \text{ cm}$ water. This solution was then analyzed for transition metals after a $4\times$ dilution with the chromatogram

TABLE I
PERCENTAGE OF TRANSITION METALS IN ALLOYS AND IN EXTRACTED ARTIFICIAL PIT SOLUTIONS

Metal	304 alloy composition	316 alloy composition	304, 1 M HCl, -0.2 V (SCE)	316, 1 M HCl, -0.2 V (SCE)	304, 1 M HCl, -0.1 V (SCE)
Cr^{3+}	18	17	7.3	7.1	10.0
Ni^{2+}	10	12	18.1	17.8	14.6
Fe^{2+}	68	65	68.2	68.0	73.4
Mn^{2+}	1.5	2.0	6.4	7.1	2.0

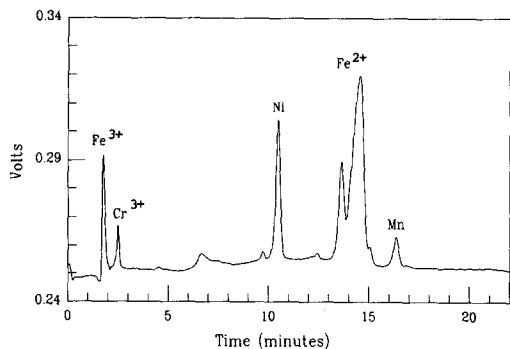


Fig. 5. Chromatogram of solution removed from artificial pit apparatus with 304 SS in 1000 mg/l sodium chloride + 1000 mg/l hydrochloric acid, +0.7 V (SCE). The splitting of the Fe^{2+} peak was found to occur with high concentrations of Cl^- in the sample.

shown in Fig. 6 resulting. The presence of Cu^{2+} indicates that this trace alloying element will dissolve under crevice corrosion conditions if the potential is high enough. It was not detected in any of the 1 M hydrochloric acid tests [$E = -0.2$ V (SCE)], indicating that the potential inside at least a portion of the crevice was sufficiently above the Cu/Cu^{2+} reversible potential to allow significant dissolution. In addition, a small amount of cobalt was detected. While not an intentional alloying addition to Type 304 SS, cobalt often enters the alloy as part of the scrap metal from which much of the Type 304 SS is now made. These results indicate that it also preferentially dissolves from the alloy under crevice

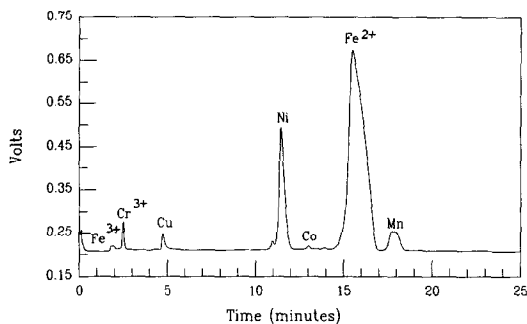


Fig. 6. Chromatogram of solution removed from actual 304 SS crevice in 1000 mg/l sodium chloride + 1000 mg/l hydrochloric acid, +0.2 V (SCE). Note the detection of Cu^{2+} and Co^{2+} , indicating preferential dissolution of these elements under crevice corrosion conditions.

corrosion conditions. The slightly distorted peak shape for the Fe^{2+} is due to the relative high concentration of this species.

CONCLUSIONS

IC has been shown to be capable of determining the transition metal content of occluded cells of stainless steels. The simultaneous analysis of iron (both ferrous and ferric), chromium, copper, nickel, cobalt and manganese is possible to the 10 $\mu\text{g}/\text{l}$ level. In this way, the relative dissolution rates of different components have been determined under both pitting conditions and uniform dissolution conditions. In neither case is dissolution stoichiometric, with Mn and Ni being preferentially dissolved and Cr preferentially retained in the alloy. In addition, it has been shown that solutions can be extracted and analyzed from crevices consisting of PTFE and 304 stainless steel.

Future work will focus on the following areas: (a) working with smaller, well-defined crevice volumes, (b) studying the effects of alloying elements such as Mo and N on the initiation and propagation stages, (c) investigating the role of the dissolution products of MnS inclusions in the initiation of crevice corrosion, and (d) extending the technique to aluminum-based and nickel-based alloys.

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