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Corrosion Protection of Aluminum Alloys by Double-Strand Polyaniline

Robert Racicot[a], Richard Brown[b], Sze C. Yang[a]

[a] Chemistry Department and [b] Chemical Engineering Department, University of Rhode Island, Kingston, RI 02881, USA

Abstract

Corrosion protection of aluminum alloys was achieved by using a double-strand polyaniline as a surface conversion coating. The effectiveness of the coating was tested by salt-spray, and immersions in salt and acidic salt solutions. Electrochemical impedance spectroscopy measurements show that the conducting polymer coated AA7075 alloy is highly resistant to corrosion. Mechanistic studies indicate that the conducting polymer is not a barrier polymer coating, but it chemically converts the surface of the alloy to form a passive layer that protects the metal from corrosion. The use of double-strand polyaniline facilitates a paintable formulation for coating and provides good adhesion to the metal surface.

Keywords: Polyaniline, Coatings, Corrosion protection, Aluminum, Chromate conversion, electrochemical impedance spectroscopy.

1. Introduction

The high-strength aluminum alloys are far more susceptible to corrosion attack than pure aluminum. These alloys need coatings or surface treatments to inhibit corrosion. Standard chromate inhibitors are effective for anticorrosion, but their toxicity is a serious environmental concern. In this article we study the potential for the electrically conducting polymer as a non-chromate corrosion inhibitor.

Although the study of conducting polymer anticorrosion coating on aluminum alloys has just begun[1,2], the studies on steel and stainless steel had been active for more than a decade[3-10]. The experimental observations indicate a strong interaction between the conducting polymer and the surface of steel.

In this article we report (1) corrosion inhibition of the high-strength aluminum alloy AA7075 by a double-strand polyaniline.

2. Double-strand polyaniline as a coating material

We have previously reported the synthesis of a double-strand polyaniline.[11-14] The double-strand polyaniline is a molecular complex of two polymers: (1) polyaniline, and (2) a polyanion. These two linear polymers are bonded non-covalently in a side-by-side fashion to form a stable molecular complex.

The advantages of the double-strand complex are the following: (1) The conductive state of the polymer is very stable because the polymeric dopant is part of a stable complex. (2) With proper choice of the polymeric dopant, the conductive polymer can be dispersed in solvents to be used as a coating material. (3) The polymeric dopant provides sites for functionalization to achieve good adhesion to metal and to the top coat.

3. Corrosion inhibition by double-strand polyaniline

The polymeric dopant used in the present study is a copolymer poly(methylacrylate-co-acrylic acid). The molecular complex with polyaniline was dissolved in ethyl acetate to facilitate coating of thin films on aluminum alloys.

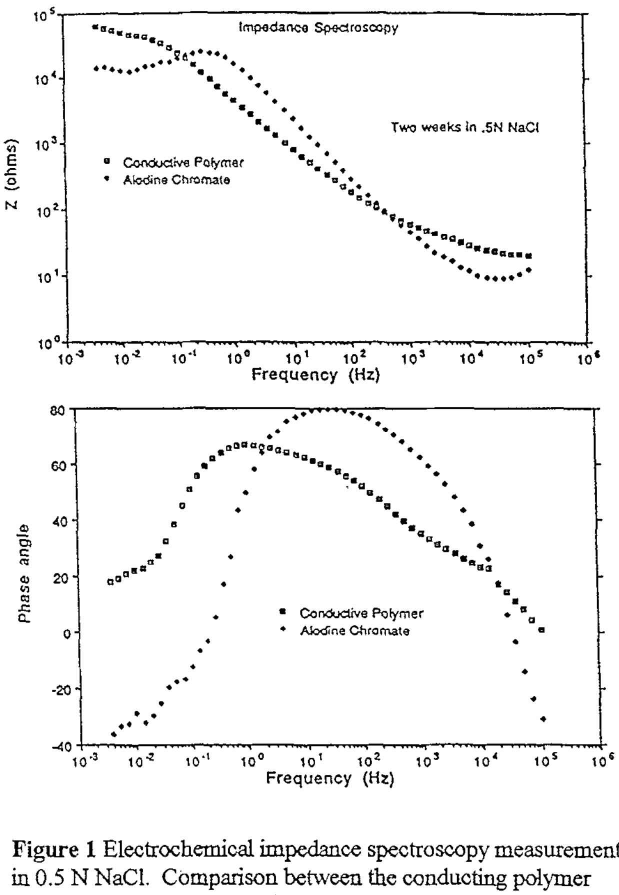

Figure 1 Electrochemical impedance spectroscopy measurements in 0.5 N NaCl. Comparison between the conducting polymer treated sample and the Alodine 600 chromate conversion samples of AA7075. The samples had been immersed in 0.5 N NaCl solution for 2 weeks at the time of these ESI measurements.

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Salt-spray tests according to ASTM B-117 show increased protection comparing to Alodine-600 chromate conversion samples. In addition to corrosion protection, good adhesion to the metal was found with no delamination. The scratched lines of the sample remain sharp after 200 hours of testing while the Alodine-600 samples show undercut and spreading of corrosion.

In another set of tests, the samples were immersed in 0.5 N NaCl solution for 3.5 months before comparative examination for pitting corrosion under the thin film of polyaniline coating. The samples show significantly less pitting than the uncoated controls. There were no overcoats used in these tests.

The Electrochemical Impedance Spectroscopy (EIS) studies suggest that conducting polymer is competitive with the Alodine-600 chromate chemical conversion. Samples immersed in 0.5 N NaCl solutions were monitored periodically by EIS. Fig. 1 shows an example of the comparison between Alodine-600 and the double strand polyaniline coatings on the aluminum alloy AA7075-T6. The low-frequdncy impedances of both coatings are high (about 10^5 ohm) indicating that the performance of the conducting polymer is comparable to that of the Alodine chemical conversion.

When the samples were exposed to the doubly corrosive solution of salt and acid (pH 3.6), the conducting polymer performs better than Alodine-600. In this acidic media, the chromate conversion coating is no longer protective and the impedance value decreased to a non-protective level. In contrast, the corrosion resistance remained high for the double-strand polyaniline coated samples. Fig. 2 shows the comparison at the initial stage (3 days) of the EIS tests in pH 3.6 buffered 0.5 N NaCl solution. For the polyaniline-converted AA7075 surface, the low frequency charge transfer resistance approaches 10^6 ohm and the impedance remains high at the time of this report (three weeks). The Alodine-600 chromate conversion sample is far less resistant to corrosion in this acidic salt environment. The low frequency impedances of these chromate samples decreases by one order of magnitude within the first three days of the test and continue to decrease to that of an unprotected sample (below 10^4 ohm).

4. Chemical conversion of the aluminum surface by the double-strand polyaniline.

We have prevously reported [1,2] experimental observations that are consistent with a reactive interaction between the conducting polymer and the aluminum alloy to form a protective layer. It should not be surprising to see reactive interactions because the electrochemical potential of the conducting polymer solution (0.3 V vs. SCE) is sufficiently anodic to oxidize aluminum (with an E_{cox} of -0.7 V vs. SCE). The rate of interfacial redox or charge-transfer reaction could be relatively high comparing with other solid coating because the material is electrically conductive. It is reasonable to consider the polyaniline coating as a replenishable oxidation agent attached onto the aluminum surface. One possible consequence of such an oxidative interaction is to build up an oxide or oxide-like interfacial layer between the conductive polymer and the metal surface. If this chemically converted interfacial layer is stable against the corrosive anions such as the chlorides, it may limit the corrosion current.

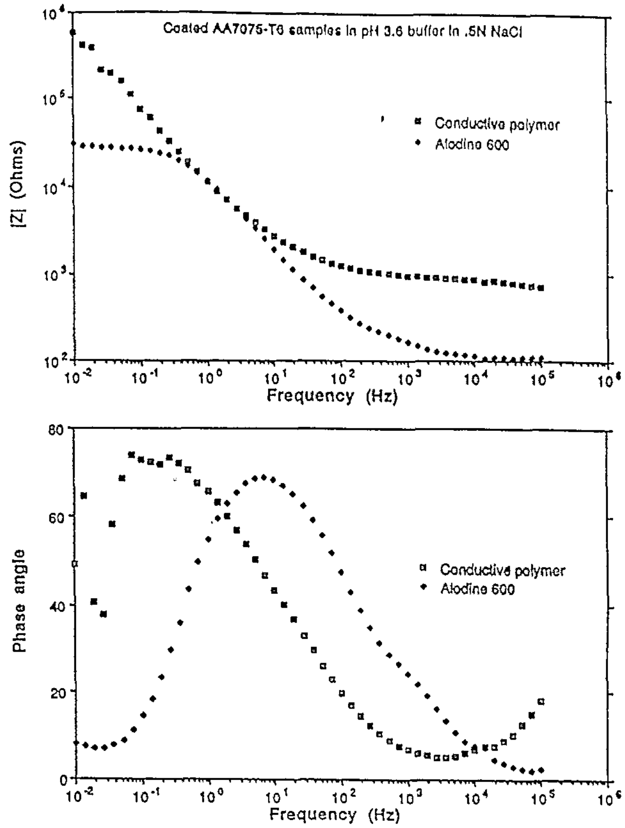

Figure 2 Electrochemical impedance data comparing two types of surface conversion coatings on AA7075 tested in acidic salt solutions (0.5 N NaCl solution buffered at pH 3.6). The sample had been immersed in the acidic salt solution for 3 days at the time of this measurement. AA 7075 suface converted by conducting polymer: □, and by Alodine-600 chromate: ◆.

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