The Corrosion Protection of Metals by Conductive Polymers. II. Pitting Corrosion

Wei-Kang Lu

Materials Science and Engineering, The University of Texas at Arlington

Ronald L. Elsenbaumer

Department of Chemistry, The University of Texas at Arlington

INTRODUCTION

It is well known that a sheet of mild steel exposed to a moisture environment within several days will rust badly with pits covered by corroded products. The most common pitting is the selective attack of surface scratch or induced breakdown of the protection film. The pitting mechanisms of aluminum and copper alloys may differ but the basic features are similar. Comparative pitting results of these three kinds of metal alloys will be made and presented. Electrochemical techniques can be used to investigate the passive film breakdown to study pitting propensities. Aluminum always undergoes a pitting problem in sodium chloride. Since oxides always exist on the surface, alloys and surface treatments may alleviate the degree of localized corrosion attack.

Film-forming polymerization of conductive polymers on electroactive metals’ and conductive polymers formulated with other polymers which have good adhesion properties to metal surfaces have been used for recent corrosion research in last decade. Among all the conductive polymers studied so far, Conquest® of DSM and Ormecon’s Corpassiv® are the first two to achieve commercial availability. Pitting corrosion happens on aluminum, steels and copper commonly and also affects the utilities lifetime tremendously due to aggressive growing pits with damaging species concentrated inside the pits. Furthermore, the mechanical properties of metallic materials can be changed in a short period. So far, no other experimental results in the area of applying the intrinsically conductive polymers to avoid or at least lessen the pitting corrosion on metals was specifically reported. The possibility of whether or not the conductive polymers prevent the pit propagation and growth in the areas of
electrolyte-exposed areas or metals under closed end pinholes of protective film is the key motive of this paper.

**EXPERIMENTAL**

The electrochemical cell setup can be seen elsewhere. The test equipment is a Gamry CMS120 software-controlled, automated digital ECN system and a Gamry PC3 potentiostat/zeror resistance ammeter was used for both CP and ECN measurements. The panels were received as 2 by 2-in. 2024, 6061 and 7075 aluminum alloys, C1010 grade carbon steel and A316 stainless steel. After appropriate surface cleaning and polishing, coupons were coated with the PANI-PET blend with a certain binder supplied from Americhem Inc. after reformulation by authors. Those compounds were used for coating application by hot dip or spray methods. Those sample materials of polyaniline blends were named AC1, AC3 and AC7 respectively. Corrpassive (zk) is a polyaniline PANI-PMMA mixture supplied by Ormecon company. Conquest (py) is solution of polypyrrole dispersion in polyurethane made by DSM Chemicals. The deaeration tests were conducted in a two neck flask with a corrosion resistant purge tube inside the used electrolyte.

**RESULTS AND DISCUSSION**

According to corrosion rate determination data in Table 1, AC1 coating material has a far lower corrosion rate through whole immersion time compared to other commercial and control sample sets. The initial and final stages of corrosion rate of purposed uncovered area for AC1 increment is negligible. Zk kept a stable corrosion tendency that is at least 100 times faster than AC1. Figures 1 and 2 indicate that there is a high agreement of pitting tendencies between ECN and CP results for AC1, AC3 and AC7. AC1 shows an extremely low pitting current density (about 10^5 less) compared to the control. AC3 reveals metastable pitting prevention at the initial stage and a subsequent pit propagation and growth pattern shows a sudden spike on the ECN spectrum which was also confirmed by microscopic examination of the inside dent region. AC7 did not produce any pitting prevention at all. The hysteresis loop and

<table>
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<th>Time/sample</th>
<th>Control</th>
<th>AC1</th>
<th>Zk</th>
<th>Py</th>
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The Corrosion Protection of Metals

Figure 1. ECN results of drilled epoxy/PAN1 blends/C101 steel in 3.5% NaCl.

Figure 2. Cyclic polarization curves of dented epoxy/PAN1 blends/C1010 steel in 3.5% NaCl (a) AC1, (b) AC3, (c) AC7.

the total accumulated charge of pitting-repassivation cycles of these three coatings exhibit the same tendencies. Both AC1 and AC3 appeared with low corresponding pitting current within narrow ranges but AC3 had been identified as passivity breakdown at reversed scan with a 10 fold amount of cycle charge during the same scale measurement. AC7 expressed a high pitting current and a tremendous amount of dissolution charge with a tendency of at least 10^5 times greater. Both ECN and CP appear similarity in the pitting description of the AC series compounds studied. It is believed that the AC1 polyaniline blend has excellent "extended" pitting protection ability to exposed dent surface as compare to the formulations of AC6 and AC7 in the saline environment.

The pitting effects of zk and py as primer layer for drilled exposed area to brine are shown in Figure 3. Without doubt, no primer layer sample demonstrated a bigger hysteresis loop region at the highest measured pitting current. It also has largest potential gap between pitting potential and repassivation potential (protection potential). Generally, zk has a best pit
prevention performance with a defined small loop at relative positive potential with a narrow potential difference. This means pitting potential and repassivation potential are close each other which has the possibility to halt pit propagation even with initial pit formation on steel surface. Figure 4 shows py had an excellent pitting passivation property even with existing pinholes through cast films covered on aluminum alloy. The bare 2024 aluminum alloy showed the onset of pitting after 1.5 hours of immersion then a plateau region. Meanwhile, zk coated 2024 aluminum alloy shows quite a variation on pitting expression: surfaces will passivate for a short time then go up to keep the original scale of measured current.

The constant phase element (CPE) can be seen from Figure 5. CPE behavior is observed from most of kinds of protective films in impedance response. One can consider the film and
dielectric interface of electrolyte/film to act like a series of complex non-ideal capacitors. Somehow, the impedance spectra correspond to porosity and localized pit activities that can be monitored. From figure 5, a random distribution of low frequency data points for zk coated 2024 Al alloy during the first day of submersion mean that active pit growth un unstabilize the signal lock, and the shield effect of Al2O3 passivation film on aluminum alloy is not as good as the zk coated one, but surface coverage and cathode/anode separation also need to be considered. However, the zk-aluminum oxides complex can increase the corrosion resistance of covered passivated films by time and charge transfer resistance maintaining an almost a fixed value and polarization resistance increased from time to time. The porosity of zk film exhibits no change and still has open-end pinholes. In order to observe the actual pitting, the peeling of protective films was done showing sparsely scattered hollow pit sites on both the aluminum alloy and carbon steel surfaces. The major difference is the refill-by-products degree of mild steel seems higher than Al. For the purposed drilled hole, because of the rougher surface at the sidewall, more pits can be noticed around the inner bottom surface with some tangling fractual sidewall and not at the edge of the film-metal interface. It is suggested that the control momentum of pitting is also the potential gradient and metallurgical preparation.

The inert gas purge tests can be helpful to understand oxygen participation in the corrosion mechanism and pitting formation mechanism. Microscopic examination was performed during momentary interruption tests for comparative samples. Visual confirmation of early stages occurred with no difference. The change of color and aggregation of passivation film on original alloy surfaces were varied compared to ambient sets in the same acidic environment. Due to the hydrogen embrittlement in oxygen-free environment, the argon gas inlet samples seem to develop some sort of erosion top layer and loosely laid on surface. After cleaning the surface, several severe deep columnar pits were spotted. However, the
passivation film of oxygen-rich (ambient) immersion samples look the same before the intermediate period then formed a more compact oxidation film to shield the carbon steel. With the comparison of surface pits at the dented area, oxygen-deficient samples show more corrosion than oxygen exposes ones. We conclude that corrosion protection of mild steel by conductive polymers in 0.1 M HCl requires oxygen input in the protection mechanism when the system turns into anodic protection mode.

CONCLUSIONS

The corrosion protection of carbon steel by conductive polymers in acidic environment proved to be efficient but cannot reduce much of the pitting trend. Furthermore, most of conductive polymers cannot achieve successful long-term corrosion prevention in artificial seawater with pitting inhibition. However, existing pitting suppression by almost all conductive polymer materials is obvious in sodium chloride solution. The newly innovated Americhem formulated polyaniline (ACl) had demonstrated very strong anticorrosion properties in both general corrosion and local corrosion in 3.5 % NaCl. On the contrary, most of commercially available materials lack protection efficiency under the same experimental condition. Considerable pitting current in drilled hole can be reduced by the application of AC 1 and are technologically important because the easy processing and coating procedures lend to satisfactory mechanical strength. However, reformulation of PAN1 mixed with binder show the pitting behaviors of ferrous and nonferrous alloys influenced by intrinsically conductive polymers can be studied by ECN, CP and EIS techniques providing more understanding of the corrosion and pitting mechanisms.

Preliminary inert gas aeration results indicate oxygen is not a factor in the early immersion period but will become important when the protection mode moves to anodic protection which was confirmed by previous Tafel slope interpretations.

ACKNOWLEDGMENTS

The authors wish to thank Dr. V. G. Kulkarni and Mr. Tim Chen of Americhem Inc. for great help in providing technical assistance and the partial financial support for this project.

REFERENCES

2 V. G. Kulkami, private communication.