USE OF AN AC/DC/AC ELECTROCHEMICAL TECHNIQUE TO ASSESS THE DURABILITY OF PROTECTION SYSTEMS FOR MAGNESIUM ALLOYS

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Abstract

One task under the U.S. Automotive Materials Partnership (USAMP) "Magnesium Front End Research and Development" (MFERD) Project has been the evaluation of methodologies for the assessment of protective capability for a variety of proposed protection schemes for this hypothesized multi-material, articulated structure. Techniques which consider the entire protection system, including both pretreatments and topcoats are of interest. In recent years, an adaptation of the classical electrochemical impedance spectroscopy (EIS) approach using an intermediate cathodic DC polarization step (viz. AC/DC/AC) has been employed to accelerate breakdown of coating protection, specifically at the polymer-pretreatment interface. This work reports outcomes of studies to employ the AC/DC/AC approach for comparison of protective coatings to various magnesium alloys considered for front end structures. In at least one instance, the protective coating system breakdown could be attributed to the poorer intrinsic corrosion resistance of the sheet material (AZ31) relative to die-cast AM60B.

Introduction

The Magnesium Front End Research and Development Project (MFERD) has been the subject of several prior reports [1,2]. In brief, the project is an international collaboration between the U.S. Department of Energy, the U.S. Automotive Materials Partnership, Natural Resources – Canada, and the Ministry of Science and Technology of the People's Republic of China, with a goal of advancing both the knowledge base and manufacturing capabilities necessary to engineer and produce magnesium-intensive automotive body substructures, similar to the all-steel baseline structure shown in Figure 1, having markedly reduced weight but with equivalent mechanical strength and durability.

One task of the MFERD Project was aimed at corrosion prevention and surface treatment for magnesium components and assemblies such as that envisioned for the front end. An objective of this task was the evaluation of various coating systems as might be incorporated in the individual components and assembled structure. Figure 2 illustrates a "model" corrosion protection system for magnesium incorporating a "pretreatment" step which includes any metal cleaning and pickling or 'activation', followed by one of several possible processes to provide an anchoring layer for the topcoat (or adhesive) which is presumed to be a polymeric coating or "paint". Various pretreatment processes for magnesium have been considered over the years [3] including conversion coating (e.g. chromating), anodizing or other electrically-based processes used to develop primarily inorganic layers with substantial surface roughness to which the topcoat or adhesive can

adhere. Considering the choices of base metal (die-casting, extrusion, formed sheet), pretreatment options, and possible topcoats or adhesives, the number of surface treating permutations is substantial. Prior work reported through TMS [4] has offered an approach to coating systems evaluation predicated on such metrics as scribe creepback and accumulation of surface corrosion deposits.

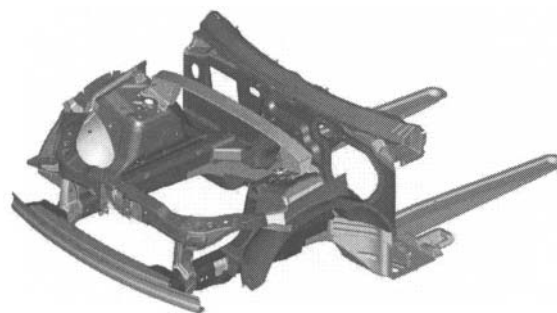### Unibody Steel Baseline Front-End Structure

Figure 1. Baseline articulated automotive front-end substructure as implemented in steel

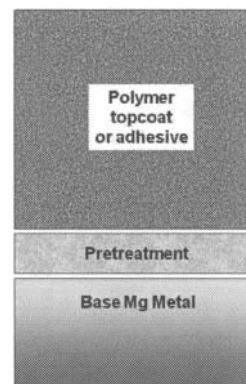### Model Corrosion Protection System for Magnesium

Figure 2. Model corrosion protection system proposed for magnesium components and front end subassembly.

Over the years, electrochemical approaches to the assessment of coatings durability have been advanced, and, in particular, the use of electrochemical impedance spectroscopy (EIS) and associated techniques. Unlike most DC electrochemistry techniques which produce substantial polarizations in excess of the unperturbed corrosion potential, EIS methods utilize only minor electrical polarizations over a wide range of frequencies, permitting an assessment of complex impedance and assignment of specific signatures to physical phenomena occurring in the "system" of the corroding workpiece and its environment. These are usually expressed in terms of electrical circuit analogs which can act as networks of capacitive and resistive elements. A simple primer on EIS methods may be found online [5].

While AC methods such as EIS offer a generally "non-destructive" probe of the state of various charge transfers occurring in coated metals in contact with an electrolyte, a more aggressive stress is required to accelerate the corrosion process for purposes of comparing the relative durability of different coating systems. Often, a cathodic reaction (i.e. electron consuming) at polymer-coated metal surfaces, leads to eventual breakdown of the attachment of the polymer to the metal permitting both undercutting of the protective polymer and concomitant corrosion of the metal. In the case of magnesium, the aqueous corrosion over a wide range of pH generates copious $Mg(OH)_2$, further aggravating polymer delamination, as well as hydrogen evolution as the principal cathode reaction, leading to increasing concentration of OH^- and further polymer delamination. Thus, DC cathodic polarization may be used to drive the polymer delamination process and accelerate the undercutting for painted magnesium. Before the delamination and corrosion product are visible, changes to the impedance spectrum can be observed, giving indications of such contributions as loss of polarization resistance at the metal surface, indicative of an increase in the corrosion process at that interface. This sequence of AC impedance measurement, followed by DC cathodic polarization and subsequent AC analysis has been referred to as "AC/DC/AC" measurement, and origins of the approach have been attributed to Hollaender, et al. [6].

The work reported here illustrates potential use of an AC/DC/AC method in the assessment of similar pretreatments and polymer coatings to differing magnesium alloys and inference of the influence of intrinsic corrosion differences of the materials on performance in these tests. Development of this, or comparable procedures, is seen as a critical tool for rapid assessment of corrosion protective coatings for magnesium.

Experimental Procedures

Materials and Surface Treatments. The magnesium materials used for this comparison were AM60B low-pressure die cast in the form of 100 x 150 x 3mm plates, and AZ31 sheet of thickness 2 mm, and comparable size. These plates were surface treated using a process line operated by MetoKote, Inc., (Lima, OH), and included alkaline cleaning, acid activation (etching), pretreatment with Henkel Alodine 5200® followed by a degassing (curing) cycle and application of an electrostatic epoxy powder topcoat (Protech KS-542-N49), with subsequent fusion. This sequence is nominally that employed commercially for current automotive front-end components [7].

Testing Procedures and Analysis. Corrosion evaluations of the two alloy forms were conducted using several techniques including:

a.) ASTM B-117 neutral salt-spray exposure with photography at 200,300,500,700 and 1000 hours, with a scribed panel,

b.) cathodic delamination according to ASTM D-1654 using 5% NaCl (per ASTM B-117) as the electrolyte, graphite counter electrode and polarization of -1.5 V vs. OCP, with photography at 500 and 1000 hours,

c.) conventional EIS using the same electrolyte and Gamry MultEchem 4 three-electrode cell, using 10 mV p-p AC voltage relative to OCP in the frequency range of 1 mHz to 100 kHz, at various times up to 35 days exposure,

d.) AC/DC/AC method (described below).

In each "cycle", the impedance of the electrochemical cell was first measured using the EIS measurement parameters described above. A cathodic DC voltage of – 4V vs. the open-circuit potential (OCP) was then applied to the sample or "working electrode" for 30 minutes to promote the cathodic reaction and presumed undercutting of the polymer film. The applied DC voltage was halted after this exposure, permitting the sample to relax to a "new" open circuit potential; this time period being two hours. The second cycle repeated the procedure, starting with the AC impedance measurement, to probe any changes of the tested sample after the previous cycle. All cycles were controlled by software using a laboratory PC. In this manner, the AC/DC/AC test generally accelerates the corrosion process. For this study, up to 30 cycles with a duration of 4 hours per cycle were typically applied. Figure 3 illustrates schematically the test cycle.
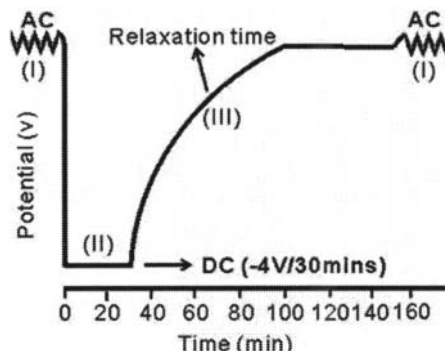

Figure 3. Schematization of AC/DC/AC polarization cycle.

The analysis of EIS spectra traditionally invokes the use of "equivalent" electrical circuit analogs such as that shown in Figure 4 for a simple coated metal in contact with a corrosive aqueous electrolyte. In the equivalent circuit suggested by Figure 4, R_s represents the resistance of the electrolyte or "solution" resistance; R_1 represents the resistance of coatings, including the pretreatment (e.g.,chemical conversion coating); C_1 represents the

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capacitance of the epoxy powder coating; R_2 represents the charge transfer resistance at the interface between the coatings and the metallic substrateor alternatively the "polarization resistance" or corrosion resistance of a metal electrode; C_2 represents the double-layer capacitance established at the interface. ZView® Electrochemical Analysis software (Scribner Associates, Inc., Southern Pines, NC), was used to record and analyze the measured data, i.e., the measured impedance at the different frequencies, and calculate the values for the simulated elements in the equivalent circuit. Plots of impedance modulus |Z|, vs frequency (i.e. "Bode") plots were also instructive in observing changes occurring during coating exposure.
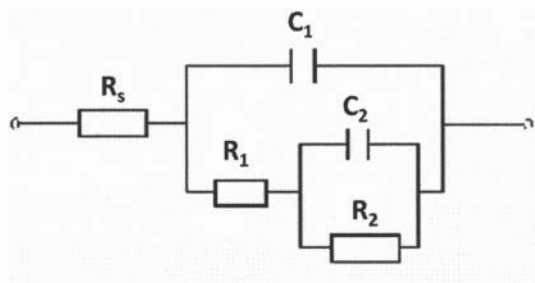
Figure 4. Equivalent circuit schematization for a corroding painted metal surface in an electrolyte.

Results and Discussion

Despite the similarity of the pretreatment and topcoating process for AM60B and AZ31 used here, the corrosion behaviors were markedly different by any of the methodologies employed; the AZ31 showing clearly inferior corrosion resistance to the AM60. This suggests that the "intrinsic" corrosion properties of the base metal, known to be poorer for AZ31 than AM60 are also manifest in the performance of the particular coating processes employed here. Because a variety of magnesium alloys are envisioned for the "front end" structure, any surface treatment and coating scheme must provide an optimized protection for all component materials, including ancillary materials of construction including other metal parts, fasteners, etc. A comparison of ASTM B-117 exposure behavior after 200 hours is shown in Figure 5. By this point, the AZ31 has already exhibited scribe undercutting or creep-back relative to the AM60 substrate.

Results of cathodic delamination studies are illustrated in Figure 6. For this testing, the AZ31 sheet exhibited pronounced paint layer debonding and corrosion at 500 hours of exposure, whereas the AM60B die cast material with comparable surface treatment showed virtually no debonding at 500 hours of exposure and beginning of noticeable debonding at 1000 hours.

Conventional EIS Bode magnitude plots for the initial and 35 day salt water exposure (5% NaCl according to ASTM B-117) of identically-treated AZ31 and AM60B are shown in Figure 7. The initial Bode plots are virtually indistinguishable suggesting that the aggregate metal and protection system are comparable. The 35

day exposure behavior does indeed, however, suggest that the AZ31 sheet material had undergone a greater loss of low-frequency impedance by about an order of magnitude. Assignment of specific circuit element impedances using the modeling software, however, did not suggest a likely candidate for this loss of impedance within the physical system.

Results of the AC/DC/AC approach as outlined are compared in Figure 8 for 27 cycles of operation as described (approximately 108 hours of exposure). While the initial Bode plots are indistinguishable (as with conventional EIS testing), the 27 cycle Bode plots now suggest a much greater loss of the initial impedance for the AZ31 sheet, by as much as three orders of magnitude. The Bode plot for the AZ31 now resembles that more of a poorly protected and corroding metal as opposed to a metal that is highly protected by the insulating polymer topcoat.
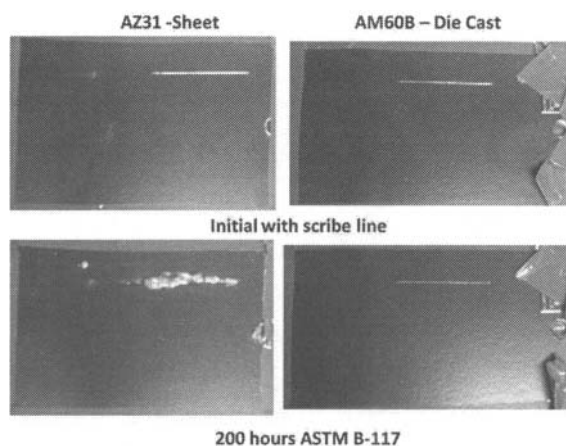

Figure 5. Compariosn of ASTM B-117 exposure behaviors for AZ31 sheet and AM60B die casting with comparable surface treatments, after 200 hours of exposure.
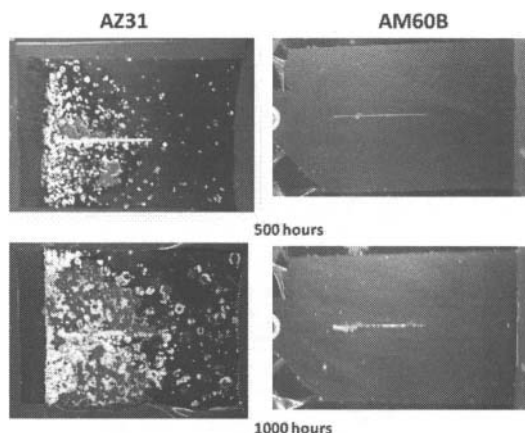

Figure 6. Comparison of cathodic debonding behavior at 500 hours and 1000 hours for AZ31 sheet and AM60B die cast magnesium with comparable surface treatments.
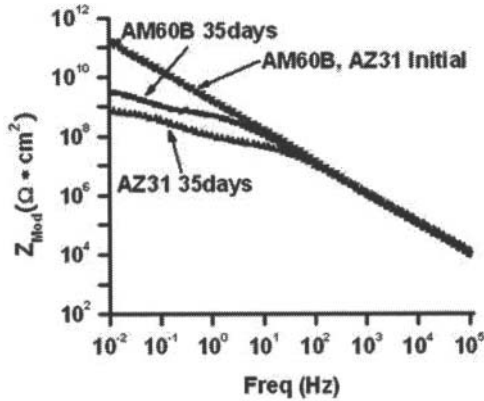
Figure 7. EIS Bode magnitude plots for AZ31 sheet and AM60B die casting with comparable surface treatments for initial measurements (indistinguishable) and after 35 day exposure to 5% NaCl solution.
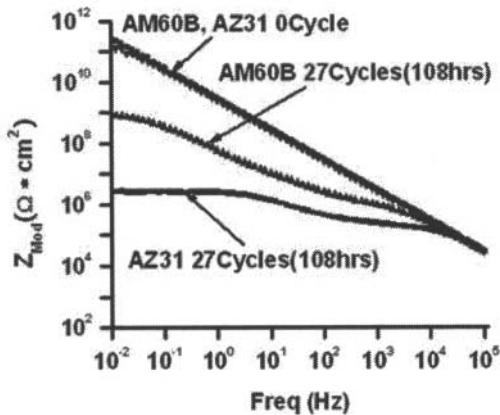

Figure 8. EIS magnitude Bode plots for AZ31 sheet and AM60B die casting with comparable surface treatments for the initial measurement and after 27 cycles of the AC/DC/AC protocol as described using 5% NaCl as the electrolyte.

Computer modeling of individual circuit elements using the AC/DC/AC protocol and presumed equivalent circuit now suggest the polarization or "corrosion" resistance at the corroding metal interface is appreciably lower for AZ31 than for AM60B. Plots of R_{cor} or "corrosion" or "polarization" resistance as a function of cycle are shown in Figure 9.In general, separate measurements of the 'intrinsic' corrosion resistance of the base metals support this observation. From a physical standpoint there is not a definitive explanation other than the poorer corrosion resistance of AZ31 in comparison to AM60, based primarily on differing aluminum content of the alloys, plus any artifacts of the processing (e.g. "skin" effects) which render the surface of AM60B either more highly enriched in aluminum or generation of appreciably levels

of non-equilibrium β-phase ($Mg_{17}Al_{12}$), exhibiting substantial corrosion resistance or having improved reaction with the conversion coating process used in this case.
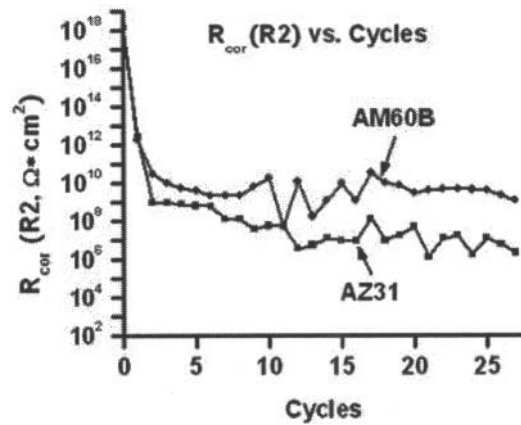

Figure 9. Plots of R_{cor} (polarization resistance) for AZ31 sheet and AM60B die casting having the same surface treatment as a function of AC/DC/AC cycle number. The situation is clearly worse for AZ31 at longer cycle times as the polymer layer and conversion coating are undercut.

In summary, the AC/DC/AC approach offers an opportunity to induce an accentuation of differences in protective capabilities of comparable processes on differing substrates, and hopefully can be developed such as to distinguish overall protective capabilities of a protection system in a rapid and quantitative fashion. Correlation of performance in such accelerated testing with actual field performance remains, however, one of the great challenges for corrosion science as applied to difficult materials such as magnesium.

References

1. A. A. Luo, E. A. Nyberg, K. Sadayappan, W. Shi, "Magnesium Front End Research and Development: A Canada-China-USA Collaboration," in Magnesium Technology 2008, eds. M. Pekguleryuz, N.R. Neelameggham, R.S. Beals and E.A. Nyberg, TMS (The Minerals, Metals and Materials Society), Warrendale, PA, 2008.

2. E.A. Nyberg, A.A. Luo, K. Sadayappan and W. Shi, "Magnesium for Future Autos," p. 35-37 in Advanced Materials and Processes, October 2008.

3. J. E. Gray and B. Luan, "Protective coatings on magnesium and its alloys – a critical review," Journal of Alloys and Compounds 336, 88-113 (2002).

4. P. J. Blanchard, D. J. Hill, G. T. Bretz and R. C. McCune, "Evaluation of Corrosion Protection Methods for Magnesium Alloys in Automotive Applications," in Magnesium Technology 2005, Neale R. Neelameggham, Howard I. Kaplan, and Bob R. Powell, eds.,TMS (The Minerals, Metals & Materials Society), Warrendale, PA, 2005.

5. Gamry, Inc.
http://www.gamry.com/App_Notes/EIS_Primer/EIS_Primer.htm.

6. J. Hollaender, E. Ludwig, S. Hillebrand, " Assessing protective layers on metal packaging material by electrochemical impedance spectroscopy," Proceedings of the Fifth International Tinplate Conference, London, (1992) pp. 300-315.

7. J. S. Balzer, P. K. Dellock, M. H. Maj, G.S. Cole, D. Reed, T. Davis, T. Lawson and G. Simonds, "Structural Magnesium Front-End Support Assembly," Society of Automotive Engineers, Warrendale, PA, Paper 2003-01-0186 (2003).