THE USE OF AC-DC-AC METHODS IN ASSESSING CORROSION RESISTANCE PERFORMANCE OF COATING SYSTEMS FOR MAGNESIUM ALLOYS

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Abstract

The potential utility of AC-DC-AC electrochemical methods in comparative measures of corrosion-resisting coating system performance for magnesium alloys under consideration for the USAMP "Magnesium Front End Research and Development" project was previously shown in this forum [1]. Additional studies of this approach using statistically-designed experiments have been conducted with focus on alloy types, pretreatment, topcoat material and topcoat thickness as the variables. Additionally, sample coupons made for these designed experiments were also subjected to a typical automotive cyclic corrosion test cycle (SAE J2334) as well as ASTM B117 for comparison of relative performance. Results of these studies are presented along with advantages and limitations of the proposed methodology.

Introduction

The Magnesium Front End Research and Development Project ("MFERD"), to which this work contributes, was recently reviewed [2]. Briefly, the project is an international collaboration between the U.S. Department of Energy, the U.S. Automotive Materials Partnership, LLC (USAMP), Natural Resources – Canada, and the Ministry of Science and Technology of the People's Republic of China. The goal is to advance both the knowledge base and enabling manufacturing technologies necessary to engineer and produce magnesium-intensive automotive body substructures with markedly reduced weight, but with equivalent mechanical strength and durability of comparator baseline steel structures.

One of several research subject matters within the ongoing MFERD Project is corrosion prevention and surface treatment for magnesium components and assemblies, particularly as envisioned for automotive substructures. An ongoing objective of the "corrosion" task has therefore been the evaluation of various coating systems as might be incorporated in both the individual component pieces and the completely assembled structure. Figure 1 illustrates a model corrosion protection system for magnesium incorporating the following elements: a.) a cleaning or preparation step, which includes any metal cleaning and pickling or 'activation,' followed by b.) one of several possible processes to provide a "pretreatment" or an anchoring layer for c.) the topcoat which is presumed to be a polymeric layer or "paint." The pretreatment process would also apply to the use of structural adhesives for joining the component pieces, or total assembly to other portions of the automotive body structures. 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 sufficient surface roughness to which the topcoat or adhesive can adhere. Considering the choices of base metal magnesium (e.g. die-casting, extrusion, formed sheet), pretreatment options, and possible topcoats or adhesives, the number of possible surface treating permutations is extraordinary. Prior work [4] offered an approach to coating systems corrosion evaluation, predicated on observable physical metrics such as scribe creepback (paint undercutting) and area fraction of accumulated surface corrosion product.
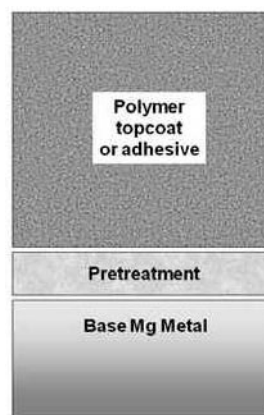
Model Corrosion Protection System for Magnesium

Figure 1. Model corrosion protection system proposed for magnesium components and front end subassembly.

The background for exploring the use of an electrochemical impedance spectroscopy (EIS) approach to the characterization of polymeric coatings on magnesium alloys and their breakdown was discussed in the earlier work [1]. A simple primer on EIS methods may be found online [5]. In the prior study, the EIS of polymer-coated metals was further extended via the use of intermittent cathodic excursions of approximately - 4 V DC (relative to the open circuit potential), for periods of 30 minutes, during a total measurement cycle of four hours. This "AC-DC-AC" approach to accelerated testing of insulating coatings has been attributed to Hollaender, et al. [6]. Cathodic polarization, particularly of ferrous materials with polymeric coatings, is a relatively common practice for assessing the resistance of the polymer layer to the localized pH transition accompanying cathodic reactions, which often generates molecular hydrogen resulting in increase of the local $(OH)^-$ concentration. This transition may be deleterious to the polymer-surface bonding. This phenomenon should certainly be considered for magnesium alloys wherein hydrogen evolution is usually the principal cathodic reaction associated with corrosion, and local stability for the magnesium corrosion product oc-

curs in basic solutions at high pH (i.e. strong base conditions). Loss of adherence of the polymer topcoat would add to the progressive corrosion of the underlying magnesium.

The previous work [1] suggested the utility of the AC-DC-AC approach for assessing behavior of coating systems in relatively short periods when compared to field exposures and manufacturer's cyclic test procedures, often lasting many months. Should such an approach be both practical and verifiable, it could be useful in sorting through the vast array of potential surface process combinations available to protect magnesium alloys. The aim of the current work was to extend the initial study to a broader array of variables in a designed experiment approach, and to continue exploration of the method as a rapid assessment tool.

Experimental Procedures

Materials and Surface Treatments. The magnesium materials used in this work were AM60B low-pressure die castings in the form of 100 x 150 x 3mm plates, provided by ACT Test Panels, Inc. (Hillsdale, MI), and AZ31 H24 sheet of thickness 2 mm, and comparable size cut from larger sheets as produced by Luoyang Copper, of Luoyang, Henan, China. Several coupons of AZ31 sheet (Magnesium Elektron) of the "benchmark" process [7] used by Ford Motor Company in a production line for F-150 radiator surrounds remained from the earlier work [1]. Unfortunately, the "benchmark" process was unavailable for the current study, and a comparable, but different "baseline" process was used instead to emulate the benchmark.

Table 1. Materials and processes considered in this work.

Designation	Material(s)	Treatments
Benchmark Process	AZ31 2mm Magnesium Elektron	acetic acid de-ox Henkel Alodine® 5200 degas Protech ES-542-N49 epoxy powder coat (commercial line)
Baseline Process	AZ31 – Luoyang Copper AM60B ACT Panels	sulfuric acid de-ox Henkel Alodine® 5200 Protech ES-542-N49 lab over bake 10 min
Designed Experiment	AZ31 (Luoyang) AM60B ACT Panels	
		Pretreatt:Alodine® 5200, sulfuric acid de-ox or AHC MagPass®
		Topcoat: Protech® Epoxy Powder, lab bake or PPG P 6000 CX cathodic electrocoat
		Topcoat thickness: typical (75µm – powder, 25 µm e-coat) or approx. 2X typical thickness.
Commercial Process	AZ31 (Luoyang) AM60B (ACT)	Alodine® 5200 PPG 590-534 cathodic electrocoat

The "benchmark" process included alkaline cleaning, de-oxidation ("activation") with acetic acid, pretreatment with Henkel Alodine® 5200 followed by a degassing (curing) cycle and application of an electrostatic epoxy powder topcoat (Protech ES-542-N49), with subsequent thermal fusion[7]. The "baseline" process also employed Alodine® 5200 and epoxy power coat, but applied in a laboratory vs. a production setting. A commercially-available coating process designed for use with aluminum and magnesium was also explored. This process included the Alodine® 5200 pretreatment (with sulfuric acid de-ox) and cathodic epoxy (PPG 590-534) electrocoat.

Table 1. summarizes the materials and nomenclature in this work. Table 2 details the layout of a 2^4 full factorial designed experiment based on magnesium alloy (AZ31 or AM60B), pretreatment process (Alodine® 5200 or AHC MagPass®), topcoat (Protech ES-542-N49 powder epoxy or PPG P-6000CX cathodic electrocoat) and coating thickness of "typical" (i.e. the usually specified coating thickness for the process) and 2X typical (produced by exposure time or current to achieve approximately twice the nominal thickness). Nominal thickness for electrocoat is usually less than 25 µm and for the powder coat 75 µm.

Table 2. Factors and levels for 2^4 full factorial design of experiments for polymeric coatings on magnesium.

Factor	(-) level	(+) level
Substrate	AZ31	AM60B
Pretreatment	Alodine ®5200	MagPass®
Topcoat	cathodic e-coat	epoxy powder coat
Thickness	nominal	2X nominal

Test Exposures and Measurement Protocols

Test Solutions. The original intent of the work was to focus on AC-DC-AC evaluation for the various materials and surface treatments when exposed to the SAE J2334 [8] electrolyte consisting of 0.5% NaCl, 0.1% $CaCl_2$ and 0.075% $NaHCO_3$ in water solution. The prior AC-DC-AC measurements [1] had been made using the 5% NaCl electrolyte according to ASTM B-117 [9]. Most manufacturer cyclic tests in use today avoid the higher NaCl concentration of ASTM B-117 in favor of lower salt concentrations as exemplified by SAE J2334, which may be more typical of actual environments to which the product is exposed. During the course of this work, however, it was found that the lower salt concentrations prolonged the degradation of coatings, to the extent that even with cathodic polarization employed to aggravate delamination of the paint layer, conditions did not permit comparisons of relative performance to be made in a reasonable time period. Later experiments employed the 5% NaCl ASTM B-117 electrolyte in hopes of securing some data in more reasonable time frames.

AC-DC-AC Protocol. EIS was employed to evaluate the barrier properties of coatings. Measurements were made using a two electrode set-up with the magnesium alloy substrate as the working electrode and a platinum mesh as the counter/reference electrode. The SAE J2334 salt solution was the test electrolyte used in all measurements. A Perspex™ cylinder with a surface area of 7.07 cm2 was mounted on the samples and was clamped with an O-ring insert to facilitate electrochemical measurements. A Gamry Instrument R 600 Potentiostat/Galvanostat/ZRA in con-

junction with Gamry Framework Version 5.20/EIS 300 software was used for these experiments (Gamry Instruments, Inc., Willow Grove, PA). Impedance response corresponding to the applied frequency of 100 kHz to 0.01Hz was measured with an acquisition rate of 10 points per decade. A 10mV amplitude perturbation potential with respect to the open circuit potential was used. In order to induce coating breakdown, the DC cathodic bias was varied to promote degradation of the coating performance. This was substantially different from the original approach [1], wherein a constant – 4V vs. OCP was employed throughout the procedure. Each DC step was applied for 4 hours during an AC-DC-AC cycle. The number of hours (where indicated) is the total number of DC hours to which the samples were subjected. While such a practice revealed which coating configurations required a greater cathodic potentials to effect a breakdown, it did not permit easy comparisons among the treatments tested, since this in itself became a variable.

SAE J2334 Cyclic Exposure and Visual Inspection. In addition to the AC-DC-AC protocol described above, scribed panels were exposed to cyclic testing as prescribed in the SAE J2334 standard [8]. This is a cyclic test protocol that exposes panels to a 24 hour cycle consisting of 100% relative humidity at 50°C for 6 hours, salt fog exposure (using the electrolyte described previously) at ambient condition for 15 minutes, and drying at 60°C and 50% relative humidity for 17 hours and 45 minutes. Cyclic testing is preferred among the auto manufacturers and was sought as a validation or confirmation of coatings performance via the AC-DC-AC protocol.

ASTM B-117 Exposures. When it became apparent that the lower NaCl concentration of the SAE J2334 electrolyte was not producing distinguishable results, particularly for the scribe creepback measurements, a decision was made to employ the ASTM B-117 5% NaCl salt fog environment as a means to provide at least some indications of the relative performance for the designed experiment matrix of Table 2. AC methods remained employable for probing of the coating impedance, with now a comparison of "before" and "after" values of the low-frequency (e.g. 0.1Hz) impedance for a 50 day exposure to the B-117 environment as the response function for the designed experiment. In this case, improved performance was indicated by a lower degree of impedance loss from the initial value. For these coupons, there was no DC bias applied to accelerate paint layer delamination. Degradation of the coating by the environmental exposure was inferred instead from loss of low-frequency impedance as a consequence of exposure to the environment. No attempt was made to assign the impedance loss to any particular equivalent circuit element (e.g. moisture ingress into the polymer dielectric layer). B-117 environment exposure also permitted a range of scribe creepback data to be obtained for the experimental array.

Results and Discussion

AC-DC-AC Measurements with SAE J2334 Electrolyte. As mentioned previously, the need to continually increase the cathodic bias levels in an attempt to force the coating breakdown was generally unsuccessful, and moreover precluded direct comparison of the various coating configurations since differing bias levels and times had been employed. Figure 2 shows the trend for low-frequency impedance as a function of DC polarization time for the "benchmark" and "baseline" coatings, using the SAE

J2334 electrolyte. The "benchmark" coating, (designated in this figure as AZ31+Al5200+PC) did not exhibit loss of impedance, despite polarizations to as much as -8V vs. OCP. The "baseline" process used to replicate the benchmark did show breakdown of the coating, both on AM60 and the AZ31 alloys. By this approach, the AZ31 actually exhibited a longer time to breakdown than had been witnessed in the prior study.

Whereas the "benchmark" process applied to AZ31 exhibited breakdown by cathodic polarization of -4 V vs. OCP when using 5% NaCl as the electrolyte, it could not be breached by as much as -8 V using the SAE J2334 electrolyte. Interestingly, however, the "benchmark" coating did exhibit appreciable scribe undercutting and creepback during exposure to the cyclic SAE J2334 testing, even though the polymer film and interface remained protective as inferred from AC-DC-AC testing. Figure 3 illustrates the degree of creepback witnessed for the "benchmark" processed coupon after 74 cycles of SAE J2334 and compared to the "baseline" coupons which suggested breakdown more readily by AC-DC-AC, but were more durable in scribe creepback.
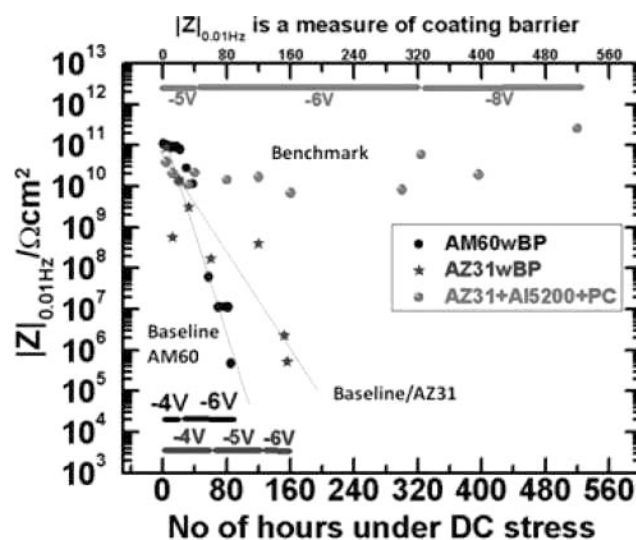
Figure 2. Loss of impedance (modulus) at low frequency (0.01Hz) in AC-DC-AC testing for hours of DC polarization at the levels shown. BP = "baseline process."
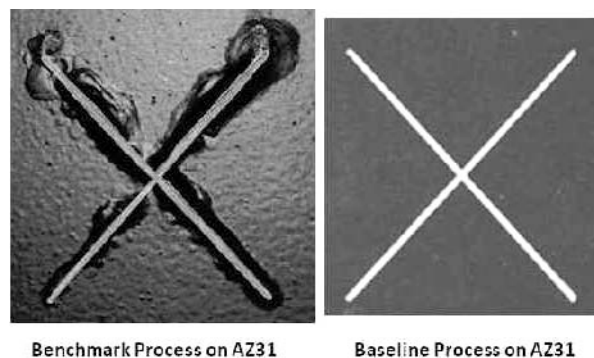
Figure 3. Scribe creepback for "benchmark" and "baseline" processed AZ31 after 74 cycles of SAE J2334.

The AC-DC-AC method probes internal changes in the coating layer and electrochemical reactions at the metal/pretreatment/polymer interface. For durable coatings, which are resistant to moisture and electrolyte ingress, the changes induced by cathodic DC polarization can be minimal. Conversely, an example of a coating which showed both a breakdown under AC-DC-AC conditions at 5 V of applied cathodic polarization, as well as breakdown in later cyclic testing (for AZ31) was the commercially-processed coating which employed Alodine®5200 as the pretreatment and PPG 590-534 cathodic electrocoat as the topcoat. Figure 4 shows a comparison of the breakdown behavior for this coating on both AZ31 and AM60 as compared to a more robust coating consisting of the AHC MagPass® pretreatment and Protech ES-542 N49 powder epoxy. Unfortunately there are no observational results at this time on cyclic performance of the latter combination.
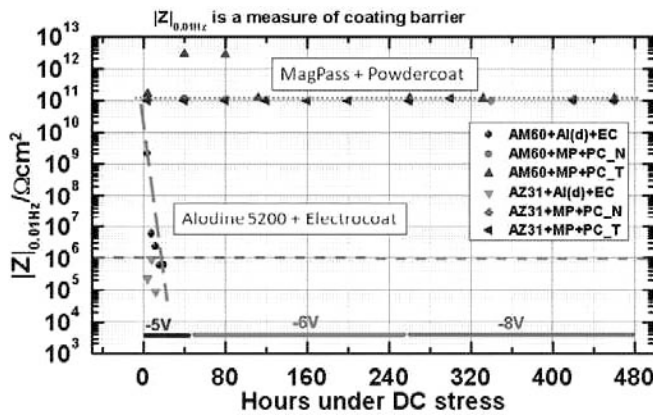

Figure 4. Impedance decay under DC stress behavior for two categories of coatings on AZ31 and AM60 – one a commercial process based on Alodine® 5200 with cathodic epoxy topcoat, and the other based on the AHC MagPass® pretreatment with powder epoxy topcoat.

Impedance Degradation with Salt Fog Exposure. It was indicated above that the AC-DC-AC methodology did not permit a ready comparison of the designed experiment matrix of substrates and coatings of Table 2 using the SAE J2334 electrolyte. This was due, in part, to the inability to produce breakdown of the particular coating configurations through cathodic polarization, even at substantial, and possibly even unreasonable potentials (e.g. in excess of -8V vs OCP). On the other hand, later experiments revealed loss of low-frequency impedance following exposures to the B-117 environment for periods of 50 days. Analysis of this data also indicated higher values for the initial layer impedance of all powder coats relative to the electrocoat of around an order of magnitude (i.e. 10^{10} for powder coats vs 10^9 ohm-cm^2 for electrocoat). It should be appreciated, however, that the low-frequency, high impedance regime is the most tenuous experimental space for precise measurement using AC methods.

Figure 5 illustrates a summary of the impedance loss (in orders of magnitude) for the initial sample, and for the same sample after 50 days of exposure to the B-117 environment. As mentioned, no cathodic polarization was employed. Table 3 illustrates the sample coding for the experiment set.

Analysis of this designed experiment set suggested, as had previously been advanced [4], that the choice of pretreatment was a significant factor in durability of the coating system. Figure 6 illustrates a "main effects" plot for this data using the statistical software Minitab®. In this particular layout, the response factor was "loss of impedance" such that lower values are preferable for more durable coating systems. For this particular designed experiment, analysis suggested that the MagPass pretreatment vs. the Alodine 5200 pretreatment had the largest effect on retention of the initial coating/system impedance, whereas the topcoat thickness had virtually no influence. Surprisingly, AZ31 sheet vs AM60 die casting showed slight improvement as did the electrocoat vs. powdercoat. Both of these results were unexpected based on prior experiments.
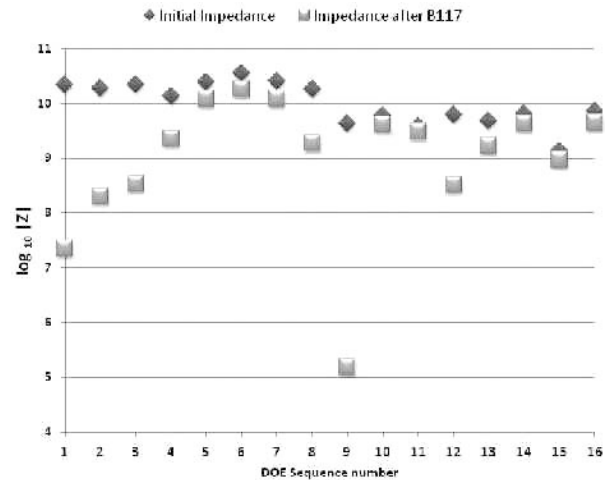

Figure 5. Summary of low-frequency initial and final impedance moduli for the designed experiment matrix of Table 2, before and after 50 days of exposure to the ASTM B-117 environment.

Table 3. Experimental nomenclature and layout for the 2^4 full factorial designed experiment of Table 2. AZ= AZ31, AM= AM60B, Al= Alodine 5200, MP= MagPass, P= powder coat, E = electrocoat, - = nominal thickness, + = 2X nominal.

No.	Base	Pretreat	Topcoat	Thickness
1	AZ	Al	P	+
2	AZ	Al	P	-
3	AM	Al	P	+
4	AM	Al	P	-
5	AM	MP	P	-
6	AM	MP	P	+
7	AZ	MP	P	+
8	AZ	MP	P	-
9	AM	Al	E	-
10	AM	Al	E	+
11	AM	MP	E	-
12	AM	MP	E	+
13	AZ	Al	E	-
14	AZ	Al	E	+
15	AZ	MP	E	-
16	AZ	MP	E	+

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No.	Base	Pretreat	Topcoat	Thickness
1	AZ	Al	P	+
2	AZ	Al	P	-
3	AM	Al	P	+
4	AM	Al	P	-
5	AM	MP	P	-
6	AM	MP	P	+
7	AZ	MP	P	+
8	AZ	MP	P	-
9	AM	Al	E	-
10	AM	Al	E	+
11	AM	MP	E	-
12	AM	MP	E	+
13	AZ	Al	E	-
14	AZ	Al	E	+
15	AZ	MP	E	-
16	AZ	MP	E	+

AZ= AZ31, AM=AM60B, Al= Alodine 5200
MP – MagPass, - – nominal thickness
+ = 2X nominal   P=Powder, E= E-coat

For the 50 day B-117 scribe creepback, a rating scale according to ASTM D1654 (0 = poor,worst; 10 = zero creepback, best) was employed. These values were also treated statistically with Minitab®. Figure 7 shows this main effects plot supporting improvements with MagPass vs Alodine 5200, AZ31 vs AM60B, and thicker vs nominal coatings. In this layout, there was not a noticeable influence of powder coating over electrocoat.
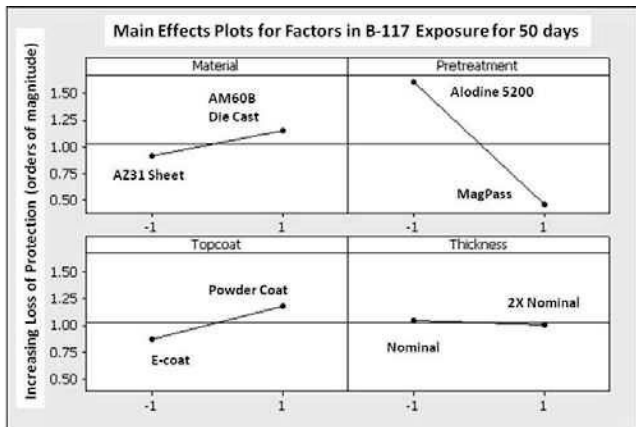

Figure 6. Main effects plot showing influence of the factors from Tables 2 and 3 on the loss of low-frequency impedance in orders of magnitude from the initial value to the final value after 50 days of exposure to the B-117 environment.
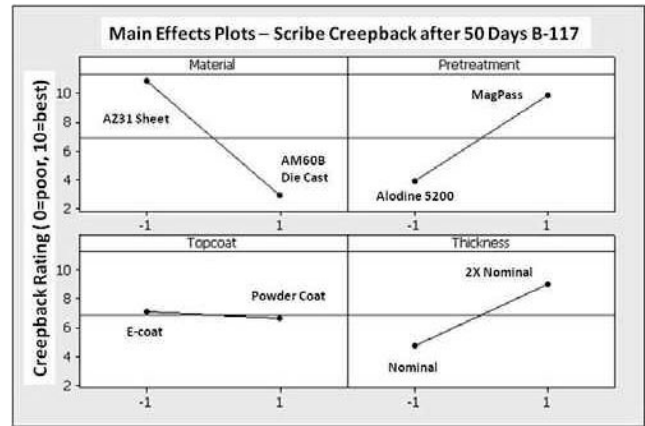
Figure 7. Main effects plot when scribe creepback rating (according to ASTM D1654) is used as the experiment response. In this scheme a higher number refers to increased resistance to film undercutting.

Summary and Conclusions

While the initial study of the AC-DC-AC approach for characterization of protective coatings on magnesium alloys was encouraging [1], the present work indicates that clearly more study is required, particularly with regard to suitable electrolytes for the measurement and also the concerns over possibly unreasonable values for cathodic polarization required to effect breakdown of the coating system – which in some instances was not achieved, even at potentials as high as -8 V vs. OCP. The one instance of a predicted rapid coating system breakdown of the commercial product at cathodic potential of -5 V vs. OCP (Fig. 4.) has been at least supported by parallel studies of the corrosion of coated assembled magnesium-intensive front-end substructures which are not detailed in this report. The use of the ASTM B-117 environment, which appeared to be needed here to effect any sort of useful measurements in a reasonable time period, is generally unattractive to automotive manufacturers as being much more severely aggressive than test environments normally employed for cyclic corrosion tests. The continuing work of the "MFERD" effort will likely also include extension to improved methods for coating system validation and comparison for magnesium alloys and magnesium-intensive subassemblies.

Acknowledgments

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