The Corrosion Protection of Magnesium Alloy AZ31B

M.D. Danford, M.J. Mendrek, M.L. Mitchell, and P.D. Torres

Marshall Space Flight Center, Marshall Space Flight Center, Alabama

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1. INTRODUCTION

Magnesium (Mg) alloys possess interesting characteristics that could affect reduced hardware mass and demonstrate cost benefits to some development programs when used in the appropriate aerospace applications. Generally, high-strength Mg alloys exhibit good fabrication characteristics with strength slightly less than most aluminum (Al) alloys and are approximately 35 percent less dense than Al alloys commonly used in aerospace structural applications today. In order to introduce the possible benefit of utilizing magnesium alloys in development and production activities, it is prudent to evaluate the character of the materials and demonstrate confidence in a material’s performance relative to proposed applications. Observations of the character of AZ31B Mg alloy (2.5–3.5 aluminum, 0.2 manganese, 0.6–1.4 zinc plus minute amounts of other metals) to corrosion susceptibility as a function of surface protection and specific environmental exposures are the topics of this discussion.

Mg is a highly active metal, commonly used for the cathodic protection of other less active metals. However, bare Mg may be used for periods of several years in a noncorrosive environment without noticeable deterioration. It is both light and strong, and may be used in place of Al, where weight is a major consideration, providing the corrosion problem is under good control. In more corrosive environments, a protective coating must be used to control the corrosion of Mg.

Three different coatings were examined in this work, namely, anodize, Dow-23™, and Tagnite™. Dow-23™ is a stannate immersion process which deposits a thin layer of tin on the magnesium surface. Tagnite is a proprietary electrolytic process similar to anodizing. The Tagnite™ used in this study was type 8200 with a Rockhard epoxy resin seal. All three of these coatings were tested using electrochemical methods and with a very corrosive environment (continuous exposure to an aqueous 3.5 percent sodium chloride solution). The Dow-23™ and bare Mg were also examined in an 80 °F, 90 percent relative humidity (RH) environment for general and stress corrosion characteristics. This environment is much less severe than those typically evaluated for corrosion control, but is significantly more severe than that typically encountered by payload projects, in which hardware is usually assembled, stored and launched in environments with less than 70 percent RH.

For the electrochemical techniques, three different methods were employed. The first of these involved a study of the localized corrosion using the new scanning reference electrode technique (SRET) apparatus, to be described in the following section. Other methods employed were the dc polarization resistance (PR) technique¹–³ and the electromechanical impedance spectroscopy (EIS) technique.⁴
2. THE SCANNING REFERENCE ELECTRODE TECHNIQUE

The SRET instrument shown in figure 1 is commercially available from EG&G Princeton Applied Research Corporation (EG&G-PARC). It has the capability to measure microgalvanic potentials close to the surface of materials, and it allows in-situ examination and quantification, on a microscopic scale, of electrochemical activity as it occurs. The SRET is microprocessor controlled, and electrical potentials are measured by a special probe capable of translation in the \( x \) and \( y \) directions. The specimen in the form of a cylinder is held in a vertical position and rotated around the \( y \) axis. The scan is synchronized with a display monitor and the resultant data are shown in the form of line scans or two-dimensional area maps. The width of the area maps (\( x \) direction) can be set at will using the zoom-in feature of the experimental setup. The height of the area maps (\( y \) direction) is set automatically by the control software according to the proper aspect ratio. Movement of the scanning probe during data collection is in the \( y \) direction. Direct measurement of surface potentials, showing anodic and cathodic areas, at discrete positions on the sample surface, may be taken and stored for time-related studies. Because the minimum detectable signal (MDS) is of the order of \( 1 \text{ mA/cm}^2 \), a potential must be applied to the sample to increase the corrosion current to at least this level, accomplished by means of a separate potentiostat (EG&G-Parc Model 273A Potentiostat/Galvanostat) coupled to the SRET system.

Figure 1. The scanning reference electrode system (A-metal sample, B-probe, C-counter electrode).
3. EXPERIMENTAL PROCEDURES

3.1 Electrochemical Methods

For the SRET measurements, samples consisted of cylindrical metal rods 10.2 cm (4 in) long. Rod diameters were approximately 1.2 cm (0.48 in), but varied slightly from sample to sample. For each experiment, the test specimen was mounted in the collet of the SRET system and the probe, counter electrode and reference electrode were placed in their proper positions in the machine. The probe was then driven to a position with the point approximately 0.5 mm (.022 in) from the metal cylinder, and the entire assembly was immersed in a corrosive medium consisting of 3.5 percent sodium chloride solution. About a 5.1 cm (2 in) length of the metal sample rod was thus exposed to the corrosive medium. A potential noble to the normal corrosion potential \((E_{corr})\) was then applied to the metal sample rod. This applied potential was different for each sample, and for most samples, was kept to a minimum value to prevent excessive corrosion of the Mg. During data collection the samples were rotated at 100 revolutions per minute (r/min). Map scans were taken beginning and ending at equal distances from the zero point of the SRET system, such that a distance of 3.0 cm (1.18 in) of the sample circumference was displayed on each map (x direction). The experiments were set up so that all maps had a width of 3.0 cm (1.18 in) (x direction) and a height of 2.25 cm (.89 in) (y direction). Movement of the probe during the scan was in the y direction. Scans for each of the three samples (anodized, coated with Dow-23™, and Tagnite™ coated) were recorded immediately after reaching a suitable current level and after a period of 1 hour. After data collection was completed, each map was displayed on the computer screen and the proper palette for display of the map features (potentials for anodic and cathodic features) was obtained using software developed by EG&G-PARC for this purpose. Strengths of the positive cathodic features and negative anodic features in millivolts (mV) were measured with the same software, and were typed on the maps in their appropriate places using other software.

Data for the determination of corrosion rates for each of the samples exposed to 3.5 percent sodium chloride were obtained using the dc polarization resistance (PR) technique. Data for this technique were collected using EG&G instrumentation and the model M347C software. The data were corrected for IR (voltage) drop during each scan. The potential applied to the specimen during the scan was varied from -20 to +20 mV on either side of the corrosion potential, and the data points (current and potential) were recorded in 1/4-mV increments. The PR data were analyzed using the program POLCURR. Corrosion currents for the bare Mg, Mg coated with Dow-23™, and anodized Mg were so large that use of the EIS method was impractical, while the currents for a Tagnite™ coated sample were too small for the more sensitive EIS technique, even after a 30-day period. Three flat plates of the Mg alloy, 7.62 by 3.81 cm (3 by 1.5 in) were grit blasted on both sides and cleaned with alcohol and acetone. One plate was left bare, while each of the other two were coated on one side with approximately 0.08 cm (3 mils) of the Dow-23™ coating and 0.023 cm (0.9 mil) of Tagnite™ respectively. The plates were clamped in three separate flat cells manufactured by EG&G-PARC, with an area of one cm² continuously exposed to a 3.5 percent sodium chloride (NaCl) solution. Corrosion currents were measured on alternate days over a period of several days by the PR technique and
converted to corrosion rates by standard methods. Each measured result represented the average of three separate determinations. Attempts were made to use the EIS technique with the Tagnite™ coating, but corrosion currents were too small to measure. However, the Dow-23™ was also studied using corrosive water (148 ppm sodium sulfate, 165 ppm sodium chloride, and 138 ppm sodium bicarbonate), which is a much less corrosive environment, using the EIS technique. Silver/silver chloride reference electrodes were used in all cases. In these measurements, data were taken in three frequency ranges. The first two ranges, beginning at 0.001 and 0.1 Hz respectively, were obtained using the fast Fourier transform technique. The data in the third range, 6.28 to 100,000 Hz, were collected using the lock-in amplifier technique. The sequencing was performed using the autoexecute procedure, with all data merged to a single set for each run. After collection, these data were processed and analyzed by computer using a suitable equivalent circuit model.

3.2 General and Stress Corrosion Testing in 90 Percent Relative Humidity

General corrosion and stress corrosion tests were conducted in a Parameter Generation and Control (pgc) model CL-5620A climate control chamber using a Watlow Micro-Pro 2000 microprocessor-based programmer. The system was programmed for continuous operation at 80 °F and 90 percent RH. Panels of Mg alloy AZ31B, 4 in × 6 in × 0.375 in, were prepared by alkaline cleaning and pickling in hydrofluoric acid. Five of the panels were rinsed and left bare while the another five were immediately immersed in the Dow-23™ coating process. Four of these panels were placed in the climate controlled chamber for a period of 140 days. The remaining two panels (one coated, one bare) were placed in an electric desiccator to serve as controls. Periodic monitoring for corrosion was conducted; initially every other day, then about once a week.

Tensile samples were machined from 0.375 in-thick plates of AZ31B Mg alloy in the long transverse direction. The AZ31B alloy was selected because it is susceptible to stress corrosion cracking. Seven samples were coated using the Dow-23™ process. Seven others were left bare. Three each of these samples were tensile tested on an MTS Universal Test Machine. The remaining samples were loaded to 90 percent of the specimen’s yield strength in a constant strain/stress corrosion test fixture used routinely in this laboratory. The average yield strength determined by the tensile testing for each group was used to determine the strain required to reach the 90 percent load. The precipitation hardening steel stress corrosion frames were then coated with Mascote No. 2, a nonconducting polymeric maskant, to isolate the specimens from any possible galvanic effects. All samples were placed in the climate controlled chamber for 140 days.
4. RESULTS AND DISCUSSION

4.1 SRET Experiments

SRET procedures were described in the preceding section. Area map scans for the bare wrought Mg alloy are shown in figures 2 and 3. The initial potential was adjusted so that the signal level was near the MDS level. As a result, the maps are slightly affected by noise, as figures 2 and 3 show. The applied potential was 150 mV noble to $E_{corr}$. After a 1-hour delay for the scan shown in figure 3, the current level had actually decreased due to passivation. The map scans show that corrosion is highly localized in the Mg alloy, with a strong tendency toward pitting. The strength of the features has diminished considerably during the 1-hour delay between scans 1 and 2, indicating that passivation has occurred.

Figure 2. Initial localized corrosion in bare magnesium alloy.
Map scans for the Mg alloy coated with Dow-23™ are shown in figures 4 and 5. These maps show far fewer and more uniform features than does the bare alloy. The current level was again adjusted to a value near the MDS level using an applied potential of 780 mV noble to $E_{corr}$. The maps are again affected by noise. As the figures show, there is a lesser tendency toward pitting, the anodic (negative) areas and cathodic (positive) areas being fewer, generally broader and more uniform than were those for the bare Mg alloy. The current level increased slightly with time, and the strengths of the anodic and cathodic features increased. Thus, the Dow-23™ coating is effective in reducing the corrosion of Mg.
Figure 4. Initial localized corrosion in magnesium alloy coated with Dow-23™.

Figure 5. Localized corrosion in magnesium alloy coated with Dow-23™ after 1 hour.
Maps of an anodized sample of the Mg alloy are shown in figures 6 and 7. The potential was set at 171 mV noble to $E_{corr}$, only slightly above that for the bare Mg alloy. Even at this low level, the initial current was quite high. Map features were highly localized and quite strong initially, but passivated considerably during the 1-hour delay between the map of figure 6 and that of figure 7. Thus, this anodizing procedure actually tends to make the metal surface more active, with a very strong tendency for pitting.

Figure 6. Initial localized corrosion in anodized magnesium alloy.
No current could be detected for a sample coated with Tagnite™ even at a high potential. This coating proved to be nonconductive and highly nonporous. Therefore, it is effective for preventing Mg corrosion even with a highly corrosive environment. The coat on anodized Mg is also nonconductive, but this coating is much more porous than that for the Tagnite™ coating.

4.2 Corrosion Rate Measurements

Corrosion rate measurements for samples exposed to 3.5 percent sodium chloride were all made using the PR method. Results are listed in table 1 for the bare Mg alloy, anodized Mg alloy, and for the alloy with the Dow™ coating. Plots of these results are shown in figure 8. For the Tagnite™ coat, there was no observable corrosion current even after a 30-day exposure, and the sample showed no evidence of any corrosion at all. These currents were also too small even for the more sensitive EIS technique.

Table 1. Corrosion rates observed by the dc polarization resistance technique.

<table>
<thead>
<tr>
<th>Time, Days</th>
<th>Bare Mg (mils/yr)</th>
<th>Anodized Mg (mils/yr)</th>
<th>Dow-23™ Coat (mils/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>945.3</td>
<td>374.1</td>
<td>53.05</td>
</tr>
<tr>
<td>1</td>
<td>249.1</td>
<td>477.0</td>
<td>94.55</td>
</tr>
<tr>
<td>3</td>
<td>96.8</td>
<td>428.3</td>
<td>85.82</td>
</tr>
<tr>
<td>5</td>
<td>73.8</td>
<td>325.4</td>
<td>139.7</td>
</tr>
<tr>
<td>7</td>
<td>112.7</td>
<td>151.7</td>
<td>104.9</td>
</tr>
<tr>
<td>9</td>
<td>76.8</td>
<td>107.2</td>
<td>135.0</td>
</tr>
<tr>
<td>11</td>
<td>90.4</td>
<td>—</td>
<td>74.1</td>
</tr>
<tr>
<td>13</td>
<td>—</td>
<td>—</td>
<td>110.6</td>
</tr>
</tbody>
</table>
Figure 8. Corrosion rates for bare Mg, Mg coated with Dow-23™, and anodized Mg exposed to 3.5 percent sodium chloride solution.

The corrosion rate for the bare Mg alloy started at an extremely high value, about 945 mils per year (mpy), but dropped rapidly to reach a steady value of about 90 mpy after 2 days. The sample was badly corroded and pitted at the end of the exposure period. The sample coated with Dow-23™ started a relatively low value (53 mpy) and remained rather steady for the remainder of the exposure period. This result indicates that the Dow-23™ coat is effective, at least in the initial stages of exposure. The Dow-23™ sample was not as badly corroded as that for the bare Mg, but had a large, rather deep pit, probably the result of galvanic interaction between the magnesium and the tin. The current for the anodized sample started at about 374 mpy, rose steadily, and achieved a level much higher than those for the bare Mg alloy and Dow-23™ coated sample before finally reaching a corrosion rate level approximately the same as those for the other two samples. The sample, after exposure, was corroded completely through, and corrosion measurements could not be made after a period of 9 days. These results are in agreement with those observed with the SRET experiments.

The Dow-23™ coating was also examined using a corrosive water environment, the composition of which was given in the experimental section. Measurements could not be made with the PR technique due to the high resistance of this medium, and corrosion rates were estimated using the EIS method. The equivalent circuit model used to interpret the data is shown in figure 9. Each of the circuit components of the model was made a parameter in a least squares refinement using the EIS Bode magnitude data (log impedance versus log ω, where ω = 2π× frequency). As expected, the corrosion rates observed were much less than those for samples exposed to the highly corrosive 3.5 percent sodium chloride solution.
A corrosion rate measurement for the bare Mg alloy was also made on the first day of exposure to this weak electrolyte using the PR technique. However, corrosion rate measurements could not be continued beyond this point, and no further measurements were made. A small decrease in the corrosion rate might be expected after the first day because of passivation. A plot of the corrosion rate measurements for the coated sample is shown in figure 10. As the figure shows, this plot generally lies lower than the level for the bare Mg alloy (about 8.5 mpy) in corrosive water, which is indicated by the dashed line figure 10. Thus, the Dow-23™ coat is moderately effective in weaker corrosive environments. A plot of the pore resistance versus time is also shown in figure 11. The high value of this parameter (about 3,500 ohms) indicates that the Dow-23™ coat also has a low porosity. However, as the results indicate, the Tagnite™ coat is the most effective for Mg, providing superior protection for long periods of time, even in highly corrosive environments. As mentioned previously, this coat is nonconductive, as is the coat for anodized Mg, but is almost completely nonporous, in contrast to that for anodized Mg.
4.3 General and Stress Corrosion Testing in 90 Percent Relative Humidity

Results from testing in the climate control chamber are shown in figures 12–14. Figure 12 shows the bare metal samples after 140 days at 80±1°F and 88±2 percent RH. The control sample is shown at
the top. Very light, localized corrosion is noted on the surface of all panels except the control. This corrosion was first noted after about 24 days exposure. The size and frequency of the corrosion pits increased over the next 2–3 weeks, then appeared to subside during the remainder of the exposure period. The corrosion pit depth on two of these localized areas was determined by mechanical removal of the corrosion product followed by measurement with a pit depth gage. One of the pits measured 0.0015 in while the other did not register any depth of penetration. Evidence of galvanic corrosion was noted where the Mg panels were in contact with the stainless steel in the climate chamber. In contrast, the samples coated with Dow-23™, shown in figure 13, showed no evidence of corrosion, except light galvanic corrosion at the edges in contact with stainless steel.

Figure 12. Bare magnesium alloy after 140 days at 80 °F and 90 percent RH (unexposed control at top).
Figure 13. Dow-23™ coated magnesium alloy after 140 days at 80 °F and 90 percent RH (coated, unexposed control at top).

Stress corrosion specimens are shown in figure 14. Note that minor corrosion was present on both the bare and the coated specimens. There were no stress corrosion failures in either the bare or coated samples after 140 days. In both sets of specimens, the frequency and area of the corrosion pits appeared to stabilize in a manner similar to the flat panels.
Figure 14. Bare and Dow-23™ coated stress corrosion specimens after 140 days at 80 °F and 90 percent RH.
5. CONCLUSIONS AND RECOMMENDATIONS

The SRET, polarization resistance, and general corrosion testing in high humidity all demonstrate that while bare magnesium has a tendency toward pitting corrosion, there is also a tendency toward passivation of newly formed corrosion pits. This effect was noted in both 3.5 percent NaCl and 90 percent RH environments. In aggressive environments, new pit formation and general corrosion lead to high rates of attack. However, bare magnesium performs fairly well in high humidity with what appears to be self-limiting pitting corrosion, while the remaining exposed area is essentially unaffected. However, the bare alloy should still be avoided for any aerospace applications in which contamination is an issue, since corrosion occurs even in noncondensing environments. Stress corrosion of moderately susceptible Mg alloys is mitigated in benign environments, owing to self-passivation of corrosion pits. In controlled environments, stress corrosion will not be a problem.

Dow-23™ is a suitable protection system for Mg alloys in benign environments. Electrochemical testing does demonstrate a slight increase in corrosion rate in harsh environments, but this effect is probably related to galvanic interaction with the tin coating. The stannate process also provides an electrically conductive surface, which would perform well in grounding applications. The protection provided by the Dow-23™ process is limited, and should only be used in applications where controlled environments are assured (70 percent RH maximum).

Anodized Mg did not perform well in electrochemical testing. It appears that once the anodic layer has been compromised, accelerated corrosion of the substrate occurs, resulting in a very unreliable system. Anodized Mg may provide good protection in more benign environments, but since it is nonconductive, would not be suitable for grounding applications. More testing would be required to demonstrate the efficacy of anodize for payload applications.

The Tagnite™ coating demonstrated outstanding performance, surpassing previously studied chromate epoxy primer/epoxy topcoat systems in electrochemical testing. The coating is nonconductive, uniform and pore free as indicated by a complete lack of impedance response. This coating will provide excellent service in most environments and when combined with Dow-23™ for electrical connections, should provide adequate protection for any payload application.
REFERENCES


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M.D. Danford, M.J. Mendrek, M.L. Mitchell, and P.D. Torres

George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama 35812

National Aeronautics and Space Administration
Washington, DC 20546–0001

Prepared by Materials and Processes Laboratory, Science and Engineering Directorate

Corrosion rates for bare and coated Magnesium alloy AZ31B have been measured. Two coatings, Dow-23™ and Tagnite™, have been tested by electrochemical methods and their effectiveness determined. Electrochemical methods employed were the scanning reference electrode technique (SRET), the polarization resistance technique (PR) and the electrochemical impedance spectroscopy technique (EIS). In addition, general corrosion and stress corrosion methods were employed to examine the effectiveness of the above coatings in 90 percent humidity. Results from these studies are presented.