

Lab Evaluation and Comparison of Corrosion Performance of Mg Alloys

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ABSTRACT

More Mg alloys are being considered for uses in the automotive industry. Since the corrosion performance of Mg alloy components in practical service environments is unknown, long term corrosion testing at automotive proving grounds will be an essential step before Mg alloy components can be implemented in vehicles. However, testing so many Mg alloy candidates for various parts is labor intensive for the corrosion engineers at the proving grounds. This report presents preliminary results in evaluating corrosion performance of Mg alloys based on rapid corrosion and electrochemical tests in the lab. In this study, four Mg alloy candidates for transmission cases and oil pans: AE44, AXJ530, MRI153M and MRI230D were tested in the lab and at GM Milford Proving Ground and their corrosion results were compared. It was found that the general corrosion performance of the alloys as measured in the lab can be ranked in the following order: MRI230D ≥ MRI153M > AE44 > AXJ530, which is consistent with the long term corrosion testing results measured via the GMW14872 test. The ranking obtained in this study can be used as a criterion in selecting alloys for Mg transmission case and oil pan applications. The study also suggests that the laboratory-based corrosion and electrochemical techniques can serve as preliminary corrosion evaluation tools in comparing the corrosion performance of various Mg alloys. After the lab evaluation, many unsuitable Mg alloys components or parts can be eliminated and thereby avoid the need for long term corrosion tests.

INTRODUCTION

The corrosion performance of Mg alloys in automotive service environments is unknown hence, driving the need for long term proving ground corrosion tests. In the face of so many new Mg alloys, it would be ideal to have a rapid, lab-

based corrosion evaluation technique in order to screen off unsuitable Mg alloy candidates and significantly reduce the number of Mg samples and parts needed for the long term proving ground corrosion tests.

This report presents some preliminary results of an effort in evaluating corrosion performance of various Mg alloys based on rapid corrosion and electrochemical tests in the lab, with the aim to correlate their lab-based corrosion behavior with their standard long term proving ground corrosion test results.

EXPERIMENTAL

MATERIALS AND SOLUTIONS

<table 1 here>

Four die-cast Mg alloys, AXJ530, AE44, MRI153M and MRI230D, were used in this study. Their nominal compositions are listed in [table 1](#).

The solutions used in this study were the solution (0.9% NaCl, 0.1% CaCl₂ and 0.075% NaHCO₃) used in the GM standard cyclic corrosion test GMW14872 [1] and the GMW14872 solution saturated with Mg(OH)₂. The solution saturated with Mg(OH)₂ is to simulate the solution after considerable amount of Mg has been dissolved into the initial GMW14872 solution during the late stages of corrosion. The dissolved Mg turns into Mg(OH)₂ and precipitate in the solution readily, which is equivalent to a Mg(OH)₂ saturated GMW14872 solution.

LAB CORROSION TESTS

The sample surfaces were polished with up to 1200 grit SiC paper. Samples were rinsed with de-ionized (DI) water and ethanol followed by drying with warm air. Samples were immersed in 1000 ml of solution at room temperature and the

hydrogen evolved during the corrosion experiment was collected in a burette above the corroding sample. The set-up has been described elsewhere [2,3,4].

GMW14872 PROVING GROUND LONG TERM CORROSION TEST

As-received die-cast plates were ultrasonically cleaned with ethanol, dried and then sent to GM Milford Proving Grounds for GMW14872 corrosion testing per the standard specifications. The corrosion morphologies of the test specimens were recorded.

ELECTROCHEMICAL MEASUREMENTS

The sample after the same surface polishing as in the corrosion immersion was immersed in the solution at its open circuit potential (OCP) for 5 min. A glass flat cell and a Solatron 1280 potentiostat system were used for polarization curve recording. Platinum gauze (25 mm × 25 mm) was used as the counter electrode and a saturated Ag/AgCl was used as the reference electrode. All potentials refer to the reference electrode in the study. The specimen was exposed to NaCl solution in the electrolytic cell at its open circuit potential (OCP) for 5 min before AC impedance measurements were conducted. During the AC impedance test, AC potential signals with amplitude of 5mV were applied, starting from a high frequency 13333Hz to a low frequency 0.033Hz. After the measurement, the specimen was left at its OCP for 2 min for further stabilization. Then potentiodynamic polarization curve measurements were carried out. Potentiodynamic polarization curve measurements were performed at a potential scanning rate of 0.1 mV/s from -0.2 V vs OCP to -1.0 V vs reference.

RESULTS AND DISCUSSION

LAB CORROSION SURFACE MORPHOLOGY

Figure 1 presents the surface morphologies of the four Mg alloys after immersion in the GMW14872 solution for 50 hours. It appears that the corrosion damage on AE44 and AXJ530 is more severe than MRI153M and MRI230D. The former two have obvious localized corrosion damage on the surfaces while the latter two do not.

HYDROGEN EVOLUTION

The variation of the corrosion resistances amongst the alloys was further confirmed by hydrogen evolution measurements (referring to Figure 2). AE44 and AXJ have much faster hydrogen evolution processes than do either MRI153M or MRI230D. Since the hydrogen evolution rate is equivalent to the corrosion rate for a Mg alloy [2, 3], the results shown in

Figure 2 actually indicate that the corrosion resistance of AE44 and AXJ is much lower than that of MRI153M and MRI230D. This is consistent with the corrosion morphology observations in this work (refer to Figure 1).

AC IMPEDANCE SPECTRA

The typical EIS spectra of the alloys are presented in Figure 3, and exhibit capacitive characteristics. According to existing corrosion knowledge about Mg alloys [5], the first capacitive loop at high frequencies should be associated with the charge transfer resistance and the non-Faradic charging and discharging process and the second one at low frequencies can be ascribed to the intermediate Mg+ formation and consumption. Therefore, the capacitive EIS behavior is a typical result of a corroding Mg alloy. Mg(OH)₂ addition did not significantly change the capacitive characteristics. This means that the corrosion products formed on their surfaces had little effect on the corrosion mechanism.

SURFACE RESISTANCE AND CAPACITANCE

From the measured EISs, the surface resistance R and surface capacitance C can be estimated, which are displayed in Figure 4 and Figure 5. Figure 4 shows that MRI153M and MRI230D have higher resistance than AE44 and AXJ530. This further supports the corrosion morphology and hydrogen evolution results (referring to Figure 1 and Figure 2). Moreover, it appears that the surface resistance of AXJ530 and MRI230 is slightly lower than that of AE44 and MRI153M respectively in corrosion performance (referring to Figure 4). Therefore, the corrosion resistance of these four alloys should be ranked in the following order: MRI230D ≥ MRI153M > AE44 ≥ AXJ530.

Another important result as shown in Figure 4 is the phenomenon that the saturation of the solution with Mg(OH)₂ led to an increased surface resistance for all the four alloys. This is understandable considering that the addition of Mg(OH)₂ can significantly increase the pH value of the solution and therefore retard the corrosion of Mg.

The surface capacitance cannot be directly associated with the corrosion process, but it can be affected by surface roughness and film thickness. From Figure 5, it seems that the capacitance of these alloys increases in the order: MRI230D < MRI153M < AXJ530 < AE44. This can be interpreted as an increase in surface roughness. More corrosion resistant alloys may have a smoother surface due to less corrosion attack. If this explanation is correct, then there is no surprise about the observation made on Figure 5 that the saturation of the solution with Mg(OH)₂ resulted in a decreased surface capacitance for the alloys, because the addition of Mg(OH)₂ made the solution less aggressive and

hence smoother surfaces. Another possible explanation for the decreased surface capacitance is that the addition of $\text{Mg}(\text{OH})_2$ led to a thicker surface film on the alloys, which may also be responsible for the increased surface resistance R .

GMW14872 CORROSION RESULTS

The original and corroded surface morphologies of the alloy plates after proving ground corrosion test are presented in [Figure 6](#). The surfaces of AZ44 and AXJ530 were much more severely corroded, resulting in a higher level of corrosion products on the surfaces than those of MRI153M and MRI230D. A further careful observation of the corroded plates revealed that the corrosion damage to AXJ530 is actually more severe than AE44 and that of MRI230D slightly milder than MRI153M. Hence, the corrosion resistance of these four alloys under the GMW14872 corrosion conditions can be ranked in the order: $\text{MRI230D} \geq \text{MRI153M} > \text{AE44} \geq \text{AXJ530}$. This order is in good agreement with previous lab immersion ([Figure 1](#)) and AC impedance ([Figure 4](#) and [Figure 5](#)) results.

POLARIZATION BEHAVIOR

The polarization curves of the alloys in GMW14872 solution and the solution saturated with $\text{Mg}(\text{OH})_2$ are presented in [Figure 7](#). These polarization curves exhibit a passivity characteristic in the anodic regions adjacent to their OCPs which is an outstanding feature that cannot be seen for Mg alloys in a relatively high concentration (eg. 5wt% or 1N) of NaCl solution. In a high concentration of NaCl solution, the anodic polarization current density usually increases dramatically as potential becomes more positive than the OCP, because the “pitting” potential of a Mg alloy is actually more negative than its OCP in the solution, thus in the anodic region the anodic current density is a localized dissolution current, which is in some sense equivalent to a pitting corrosion current [6,7]. In this study, the “pitting” potentials of all the alloys are much more positive than their OCPs (referring to [Figure 7](#), on the anodic polarization curves, the “pitting” potentials are those at which the anodic current densities suddenly increase with polarization potential). The significantly enhanced “pitting” corrosion potentials above the OCPs of the alloys should be ascribed to the mild corrosivity of the GMW14872 solution compared with that of the high concentration of NaCl solution.

Apart from the “pitting” potentials, another important finding from these polarization curves is the difference in anodic current densities. In the GMW14872 solution, the anodic current densities on the polarization curves adjacent to the OCPs of the alloys (below the “pitting potential”) have different values and can be ranked in the following order: $\text{AE44} > \text{AXJ530} > \text{MRI153M} > \text{MRI230D}$. This order only slightly changes in the solution saturated with $\text{Mg}(\text{OH})_2$: $\text{AXJ530} > \text{AE44} > \text{MRI153M} > \text{MRI230D}$. These different

anodic current densities provide an electrochemical explanation for the difference in corrosion performance of these alloys. The higher corrosion resistance of MRI153M and MRI230D can be attributed to their greater passivity as compared to AE44 and AXJ530.

Moreover, from the anodic polarization curves, we may even estimate the galvanic corrosion performance of the alloys. At an anodic potential far away from their OCPs (for example at -1.3V), the anodic current densities have the following order: $\text{AE44} > \text{AXJ530} > \text{MRI153M} \approx \text{MRI230D}$ in the GMW14872 solution and $\text{AXJ530} > \text{AE44} > \text{MRI230D} > \text{MRI153M}$ in the GMW14872 solution saturated with $(\text{OH})_2$, suggesting that MRI153M and MRI230D are better than AE44 and AXJ530 in terms of their galvanic corrosion resistance. Certainly, this prediction needs experimental verification, which will be presented in subsequent report.

JUSTIFICATION OF LABORATORY ELECTROCHEMICAL EVALUATION

It appears that the lab corrosion evaluation results (referring to [Figure 1, 2](#) and [4](#)) have a good correlation with the Milford Proving Ground corrosion test results (referring to [Figure 6](#)). If this correlation holds in theory, it would be an exciting outcome of this study and in future, preliminary evaluation and comparison of Mg alloy components can be rapidly conducted in the lab, which should screen off many unnecessary Mg alloy candidates sent to MPG for long term corrosion tests.

Due to the “anodic hydrogen evolution” at potentials above the “pitting” potential, it has been theoretically and experimentally demonstrated that electrochemical measurement of a Mg alloy in a relatively high concentration of NaCl solution may yield a misleading corrosion rate result [3,6]. Fortunately, GMW14872 solution has a low concentration of NaCl and more importantly mixing with NaCl_2 and NaHCO_3 which can to some extent suppress the detrimental effect of NaCl [8]. In such a relatively mild solution, all the alloys exhibit a kind of passivity and have enhanced “pitting” potentials above their OCPs. Therefore, the “anodic hydrogen evolution” did not occur, and thus the corrosion rate in theory can be estimated by electrochemical techniques according to the traditional electrochemical principles.

Based on the above, it is important to carry out polarization curve measurements first to ensure that the “pitting” potential is above the OCP. This should be a precondition for using the electrochemical method to evaluate the corrosion performance of a Mg alloy in the lab. If this requirement cannot be met, the electrochemical measurements will generate misleading corrosion rate estimations. In that case, only the immersion and hydrogen evolution can be used in the lab to evaluate the corrosion performance for Mg alloys.



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SUMMARY

The above results suggest that in the lab immersion, hydrogen evolution and electrochemical techniques measured corrosion performance of AE44, AXJ530, MRI153M and MRI230D can be ranked in the order: MRI230D>MRI153M>AE44>AXJ530. This is consistent with the order based on the GMW14872 long term corrosion testing results. More importantly, the lab experiments can be preliminarily used to evaluate and compare the corrosion performance of various Mg alloys.

REFERENCES

1. GM Worldwide Engineering Standards, GMW14872, Cyclic Corrosion laboratory Test, Nov. (2006)
2. Song G., Atrens A., StJohn S., Nairn J., and Li Y., (1997). Corrosion Science, 39 (5): 855-857
3. Song G., (2005) Advanced Engineering Materials, 7 563-586
4. Song G., "Effect of Tin Modification on Corrosion of AM70 Magnesium Alloy", R&D-11716, March 31 (2009)
5. Song G., Atrens A, StJohn D. H., Wu X., Nairn J., (1997) Corrosion Science, 39(10-11), 1981
6. Song G., "Corrosion and protection of magnesium alloys", Chemical Industry Press, Beijing, 2006
7. Song G., Atrens A., StJohn D., Wu X., and Nairn J., (1997) Corrosion Science, 39(10-11), 1981-2004
8. Song G., StJohn D., (2004) Corrosion Science, 46 1381-1399

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