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“ELECTROLESS” E-COATING FOR MAGNESIUM ALLOYS

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Abstract

By utilizing the unique electrochemistry of Mg, a thin organic film can rapidly be deposited on the surface of a Mg alloy by dipping the Mg alloy in a cathodic E-coating bath solution without applying a current or potential. The self-deposited coating is selectively formed on Mg alloy surfaces. Although the “electroless” E-coating pre-film is relatively thin, it can offer sufficient corrosion protection for Mg alloys in a chloride-containing environment. The stability of the film can be significantly improved after curing. The corrosion resistance of the substrate Mg alloy has an important effect on the corrosion protection performance of the coating. The coating is more protective on a corrosion resistant Mg alloy than on a non-corrosion resistant Mg substrate. The coating protection performance is also influenced by the substrate surface condition or pre-treatment process. Wet cleaning + heat-treatment may be a cost-effective surface preparation/treatment for the “electroless” E-coating in industrial applications.

Introduction

In the automotive industry, the demand for fuel efficient vehicles is currently driving the application of light materials. Magnesium alloys are potential alternative materials to steel and aluminum alloys in vehicles for the purpose of mass reduction. In addition, Mg alloys have many advantages in the automobile application, such as high mechanical strength, no toxicity, great damping capability, excellent casting fluidity, and low heat capacity [1,2]. However, the poor corrosion performance of Mg alloys is currently a challenge to the automotive engineers. Coating is one of the most cost-effective corrosion protection measures. Currently, the auto industry is looking for robust coatings for magnesium alloys in order to significantly improve their resistance to corrosion attack in automotive applications.

Many coating techniques have been proposed or developed for Mg alloys [1, 2]. In the automotive industry, application of an organic coating is a critical process in vehicle production. In the multi-layer auto coating system, the organic coating layer is expected to be the major barrier layer against corrosion attack. E-coating is a well known and the most popular coating on car bodies. It has excellent corrosion resistance and great covering ability on complex metallic components. However, it requires precise electrical control and expensive bath maintenance. If a coating similar to E-coating can be deposited on car bodies without application of a current or voltage, a significant cost reduction will result in the vehicle production, and current/voltage related issues in the traditional E-coating process may be avoided.

GM recently came up with an “electroless” E-coating technique for Mg alloys. It has been theoretically and experimentally verified that such a coating can be formed and can have good corrosion protection performance [3,4].

This paper briefly reviews such an “electroless” E-coating process that can rapidly (in a few seconds) form a thin E-coating on a Mg alloy surface from a cathodic E-coating bath without application of a current or potential. This new coating technique for Mg alloys may be used in many other industries, too.

“Electroless” E-coating Process

Basically, the “electroless” E-coating is a dipping process. An abraded/ground Mg alloy coupon is dipped into a cathodic E-coat bath solution (for example, a typical bath has a main composition: water 71-82 wt%, epoxy resin 16-26 wt%, titanium dioxide 1.3 wt%) for a short period of time (for example, 5 seconds). The immersion time can be adjusted according to the coating thickness requirement. In order to obtain a stain-free surface, the Mg alloy specimen should be slowly pulled out of the solution, so that the E-coating bath solution can flow from the specimen surface back to the bath. A coating film immediately forms on the Mg alloy surface while the specimen is being dipped/pulled out of the bath. The photos in Fig.1 show the “electroless” E-coating process. In Fig.1(a), the dry-abraded AZ91D has a shining surface before dipped into the bath. After pulled out of the bath, its surface becomes dry immediately while the excess solution is flowing back to the bath (see Fig.1 (b)). The dried surface is uniformly duller than its original surface (see Fig.1 (c)).

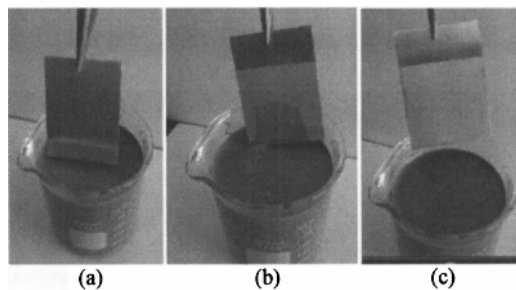


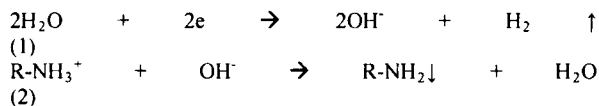
Figure 1. “Electroless” E-coating formation on a Mg alloy (AZ91D) dipping in a cathodic E-coating bath solution. (a) Before dipping; (b) being pulled out after dipping; (c) about 30 seconds after dipping.

The film rapidly formed on the Mg alloy surface after being dipped is in nature an E-coating layer. It can be cured just like a normal E-coating. For example, curing can be performed in an oven at 171°C for 25 minutes. After curing, the “electroless” E-coating is fully polymerized and has the same basic properties as a commercial E-coating.

Coating Mechanism

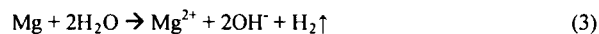
The “electroless” process follows the same coating deposition mechanism as a normal E-coating.

During cathodic E-coating, the following reactions are always involved [5,6,7,8]:



in which R-NH_3^+ is an aminoepoxy resin dissolved in the E-coating bath. Cathodic reaction (1) generates hydroxyls, resulting in an increase in pH value at the cathode surface. Reaction (2) is an E-coating pre-film deposition or coagulation step, in which the ammonia bearing organic R-NH_3^+ reacts with OH^- from reaction (1) and becomes an insoluble organic deposit (R-NH_2) on the cathode surface. After curing, the E-coating pre-film polymerizes and turns into a stable insoluble hydrophobic film. In these steps, the critical species is OH^- . As long as a sufficient amount of OH^- is provided, reaction (2) will continue and an E-coating pre-film be formed.

Mg surface always has high alkalinity in an aqueous solution because of its reaction with water:



This is a rapid alkalization reaction. It generates a sufficiently high concentration of OH^- on the Mg surface to trigger reaction (2), resulting in deposition of the E-coating pre-film there. Therefore, no reaction (1) is required, and thus the coating process is electroless.

Selective Coating for Mg Alloys

The above “electroless” E-coating mechanism predicts that the coating can only occur on Mg surfaces. Steel, galvanic steel or Al cannot generate sufficient OH^- . Thus, an “electroless” E-coating pre-film will not be formed on their surfaces.

In experiments, it has been found that the surfaces of steel, galvanic steel and Al coupons are wet for a long time or could not be dried quickly like an AZ91D coupon after being pulled out of the E-coating bath. After being washed in distilled water, their surfaces simply return to their original states; no noticeable coating remains on their surfaces.

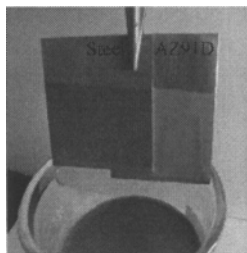


Figure 2. The abraded surfaces of steel and AZ91D coupons 10 seconds after being dipped in and pulled out of an E-coating bath.

Figure 2 show a comparison between steel and Mg alloy coupon surfaces after being pulled out from a baker containing a cathodic E-coating bath solution. The steel and Mg alloy (AZ91D) coupons were dipped in a cathodic E-coating bath together. About 10 seconds after they were taken out the bath, half of the dipped AZ91D surface area already became dry, while the whole dipped surface of the steel was completely wet. After 30 seconds, the AZ91D surface was completely dried, but the steel surface was still wet. The drying process is a phenomenon of the “electroless” E-coating deposition. Similar results have also been obtained from comparison between the Mg alloy and an Al alloy or galvanized steel. The quickly drying process selectively occurring only on Mg alloy surfaces after dipping in an cathodic E-coating bath further confirms the “electroless” E-coating deposition mechanism.

Coating Thickness

According to the proposed “electroless” E-coating mechanism, the coating growth rate should be decreasing with dipping time, and the coating cannot be very thick. This is because that after the first layer of the “electroless” E-coating pre-film is formed on a Mg alloy surface, the diffusion of OH^- through the film to meet the R-NH_3^+ from the bath is limited. The diffusion becomes slower and slower as the film grows.

The pre-film of “electroless” E-coating in theory is porous, just like a normal E-coating. The pores can be the intervals between R-NH_2 molecule trains. They are not straight holes through the pre-film from the substrate/pre-film interface directly to the pre-film/solution interface, but sinuous in the film. During an “electroless” E-coating deposition process, alkalization reaction (3) mainly occurs at the substrate/pre-film (m/f) interface. The alkalization reaction can easily proceed because of the presence of sufficient water in the pores of the pre-film next to this interface. The alkalization reaction can readily make the concentration of OH^- reach the saturated level of $\text{Mg}(\text{OH})_2$ at this interface. At the film/bath solution (f/s) interface, the supply of R-NH_2 is much easier than at the m/f interface. R-NH_2 has a relatively large organic molecule which is more difficult to penetrate or transfer than a hydroxide ion in a pre-film. Therefore, pre-film deposition reaction (2) mainly occurs at the f/s interface, and the growth of the pre-film should be controlled by the diffusion of OH^- through the film from m/f interface to the f/s interface.

Based on the above reasonable assumptions, the dependence of the pre-film thickness L on dipping time t can be deduced [3,4]:

$$L = Kt^{1/4} \quad (4)$$

where K is a constant determined by diffusion coefficient of OH^- in the film, film formation reaction constant, porosity and pore sinuosity of the film. This growing kinetics predicts that the film growth rate decreases gradually with dipping time, which is supported by experimental film thickness measurements (see Fig.3). In Fig.3, the experimental power value of dipping time is 0.24, very close to the theoretical value $1/4$.

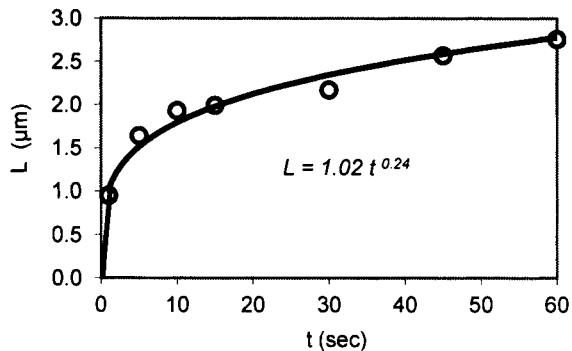


Figure 3. The growth of pre-film of "electroless" E-coating in bath [3,9].

Coating Microstructure

The deposited pre-film on Mg is porous. This is an assertion inferred from existing understanding of the commercial E-coating microstructure. It is also an assumption based on which the film growth kinetics (equation (4)) is deduced. In fact, the porosity of the "electroless" E-coating is an experimentally confirmed result. Fig.4 shows the microstructures of cured and uncured "electroless" E-coatings on AZ91D. The pre-film before curing does not appear to be dense. There are numerous tiny micro-pores in the pre-film. After curing, the number of tiny pores reduces, but relatively larger micro-pores form. These micro-pores are defects where corrosion could be initiated. The coating porosity suggests that the film formation and growth models proposed earlier are reasonable.

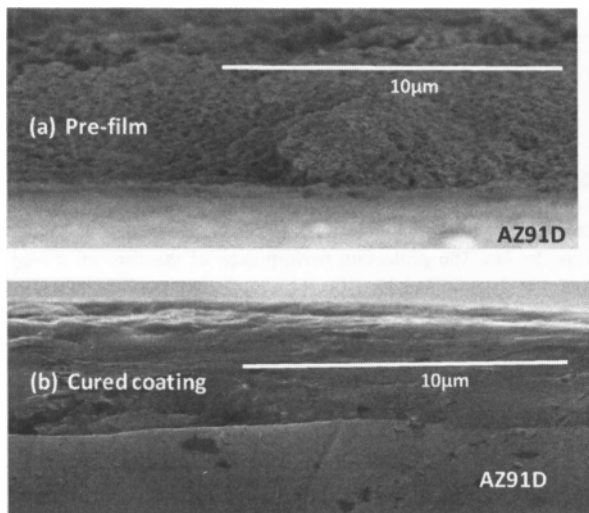


Figure 4. Microstructures of (a) the pre-film of "electroless" E-coating and (b) cured "electroless" E-coating [9]. The pre-film was formed on SiC paper abraded AZ91D dipped in the bath for 1 min. The cured coating was obtained at 171°C for 25 min.

The porosity of a pre-film could result from hydrogen evolution (equation (3)) during the film deposition process. The polymerization of the pre-film during the film curing process is

normally accompanied by evaporation of solvent and release of H₂. This also leaves porosity in the film. Thus, a cured "electroless" E-coating is also porous.

Coating Protection Performance

Since the pre-film consists of insoluble R-NH₂, it should offer a certain level of corrosion protection for its substrate if it uniformly covers the substrate. Even though the film is porous, the presence of the film on a Mg alloy surface can to a great extent retard the ingress of aggressive species and separate the substrate from corrosive environments. Hence, improved corrosion resistance of a Mg alloy by the pre-film can be expected. Curing actually turns the pre-film into a polymer coating, which is very stable material in most natural solution. Thus, curing can dramatically stabilize the coating and further enhance the corrosion resistance of a coated Mg alloy.

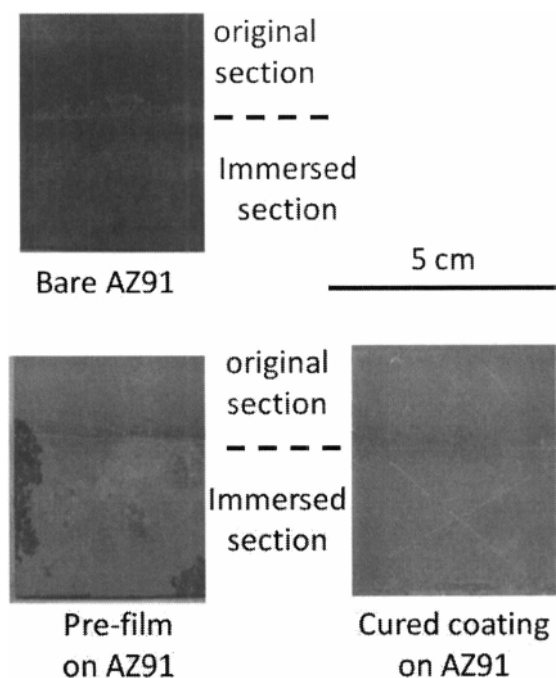


Figure 5. Corrosion damage of bare, pre-film and cured coating coated AZ91D after immersion in 5 wt.% NaCl for 24 hours [9]. The cured coating was obtained at 171°C for 25 min.

Fig.5 presents corrosion morphologies of bare, pre-film and cured coating coated AZ91D after immersion in 5 wt.% NaCl for 24 hours. It shows that the bare AZ91D is badly corroded in the whole immersed surface; the "electroless" E-coating pre-film covered AZ91D has film-damage in some areas of the immersed surface; there is no corrosion damage at all on the AZ91D surface covered with a cured "electroless" E-coating. These experimental results demonstrate that the "electroless" E-coating pre-film can effectively protect a Mg alloy from corrosion attack in 5 wt.% NaCl solution, and curing can greatly further improve the corrosion protection performance of the "electroless" E-coating. It should be noted that both the pre-film and cured "electroless" E-coating have been scratched before corrosion tests. No

preferential corrosion damage occurs along these scratches. This is an attractive feature of this coating in applications.

Corrosion of a Coated Mg Alloy

It is interesting that the porous “electroless” E-coating on a Mg alloy surface does not lead to a severe localized or pitting corrosion damage (see Fig.5). This can be explained by the corrosion mechanism of a coated Mg alloy as illustrated below.

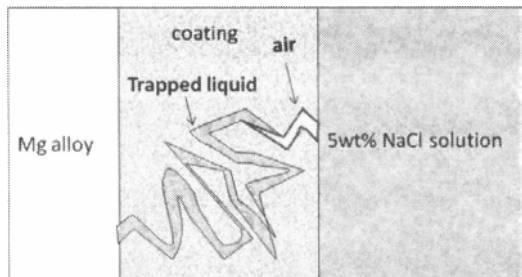


Figure 6. Schematic illustration of a pore partially filled with solution [4].

After an “electroless” E-coating formed on a Mg alloy surface and dried in air, a certain amount of water evaporates from the film pores. When the specimen is immersed into a 5wt% NaCl solution, due to the presence of some trapped air in the pores, the continuity between the liquid remaining in the pores and the bulk NaCl solution will be interrupted. This can result in a hydrophobic interface formed between the coating and the bulk environmental solution. In this case, the ingress of aggressive species from the environmental solution is interrupted by the discontinuity of the pore liquid. This discontinuity caused by trapped air is schematically illustrated in Fig.6. Therefore, an “electroless” E-coating, even though porous, can offer great corrosion protection for a substrate Mg alloy.

In some pores, the pore liquid may finally become continuous and initiate the corrosion of the substrate. Hydrogen bubbles generated from the corroding substrate will be trapped in the pores and quickly block liquid paths again. Therefore, the corrosion is unlikely to continue in the same pore. This may explain the phenomenon that the corrosion damage is not localized on an “electroless” E-coating coated Mg alloy surface. It should also be noted that the formed pre-film or cured coating is an insulating layer. Even after they are broken and the substrate Mg alloy is exposed in some local areas, there is no galvanic effect between the coatings and substrate. In other words, the undamaged coat will not accelerate the corrosion of the substrate in the broken areas. This is another reason why the corrosion damage does not appear to be localized.

Coating on Various Mg Alloys

Reactions (1) through (3) can occur on any Mg alloy surface. However, the reaction rates may vary from alloy to alloy. It is expected that the “electroless” E-coating pre-films formed on different Mg alloys may be slightly different. Fig. 7 presents such a slight difference in the pre-film thickness (L_{coat}) on 8 different Mg alloys.

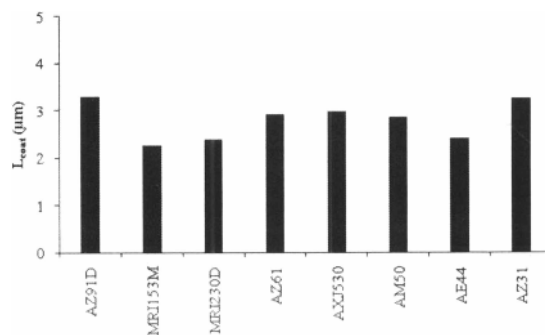


Figure 7. Pre-film thickness on Mg alloys [10].

The pre-film covered Mg alloys show significantly different corrosion performance. The corrosion damage areas of the pre-films on different Mg alloys after immersion in 5 wt.% NaCl solution for 56 hours are shown in Fig.8. It appears that the coated AZ91D is the most corrosion resistant, while the coated AXJ530 the worst in corrosion behavior.

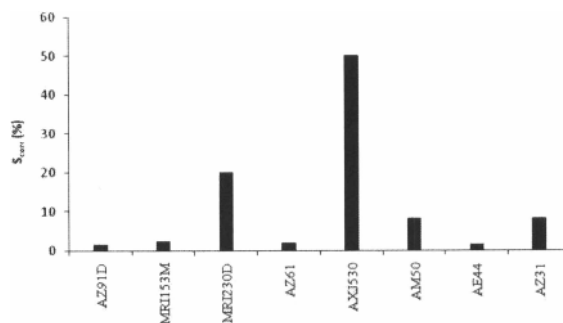


Figure 8. Corrosion damage areas (S_{corr}) of pre-film coated Mg alloys after immersion in 5 wt. % NaCl solution for 56 hours [10].

The variation in corrosion resistance of pre-film covered Mg alloys cannot be simply ascribed to the alloying elements of the substrates that may be dissolved and included in the deposited films. In fact, the protection performance of the film on a Mg alloy can be affected by film thickness, film porosity and the corrosion resistance of the substrate. Among these factors, the corrosion resistance of the substrate could be the most critical one.

For example, Fig.9 shows that the corrosion damage areas of the films on the 8 Mg alloys have a good relationship with the corrosion weight loss of the bare substrates. This is actually understandable according to the corrosion model proposed in Fig.6. Since corrosion mainly initiates from the substrate exposed to aggressive solution in the film pores, the corrosion resistance of the substrate can certainly to a great degree influence the corrosion performance of the Mg alloy underneath the coating.

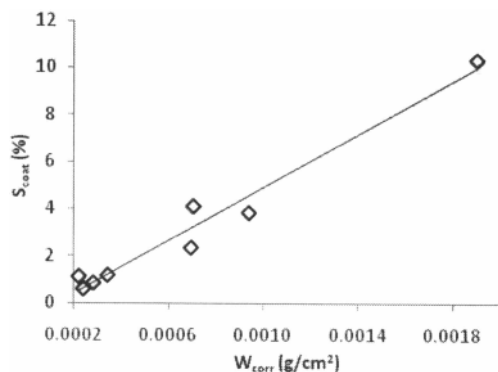


Figure 9. The relationship between the corrosion damage area (S_{coat}) of coated Mg alloys after 56 hours of corrosion immersion in 5 wt.% NaCl solution and the weight loss (W_{corr}) of corresponding substrate bare Mg alloys after 32 hours of corrosion immersion in the same NaCl solution.

Surface Preparation Effect

The surface condition can also significantly affect reactions (1) through (3) and thus will influence the coating quality. Different surface pre-treatments have been tried on Mg alloys for the “electroless” E-coating process. For example, it has been found that dry grinding/abrading can produce a good surface for this coating in terms of the coating protection performance. Sandblasting of the substrate is detrimental to the coating quality. Polishing in non-aqueous media does have a beneficial effect on the coating formation.

Among these trial experiments, there is an interesting finding: heat-treatment not only alters the corrosion resistance of the substrate, but also has a beneficial effect on the “electroless” E-coating quality. Fig.10 shows that wet-abraded AZ31 Mg alloy with heated and un-heated surfaces after “electroless” E-coating and curing has very different corrosion damage areas in 5 wt.% NaCl solution.

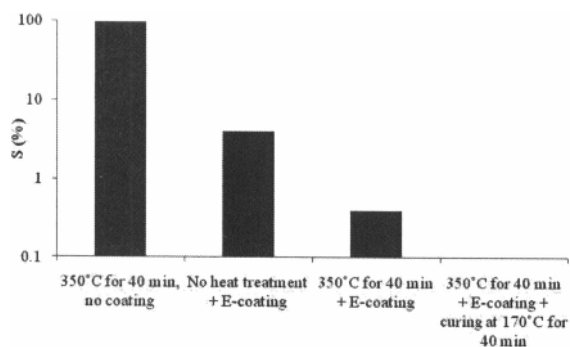


Figure 10. Corrosion area of bare and “electroless” E-coated AZ31 after 24-hour immersion in 5 wt.% NaCl solution. All the AZ31 samples were wet-abraded.

The beneficial effect of heating after abrading on coating protection performance is obvious. As heat-treatment deteriorates the corrosion resistance of AZ31D [11], this beneficial heating

effect on the coating cannot be associated with the corrosion resistance variation of the substrate, but probably be ascribed to the influence of Mg oxides on the “electroless” E-coating formation, which is currently under investigation in the lab.

An acid cleaned Mg alloy surface if pre-treated differently can also result in a different coating quality. For example, if simply etched in 10 wt.% H₂SO₄, AZ31 is not very corrosion resistant (see Fig.11 (a)). Application of a “electroless” E-coating pre-film on the etched and dried surface can significantly improve the corrosion performance (see Fig.11 (b)). If the surface after etching is heated before “electroless” E-coating, the corrosion resistance of the coated AZ31 can be further strikingly enhanced (see Fig.11 (c)).

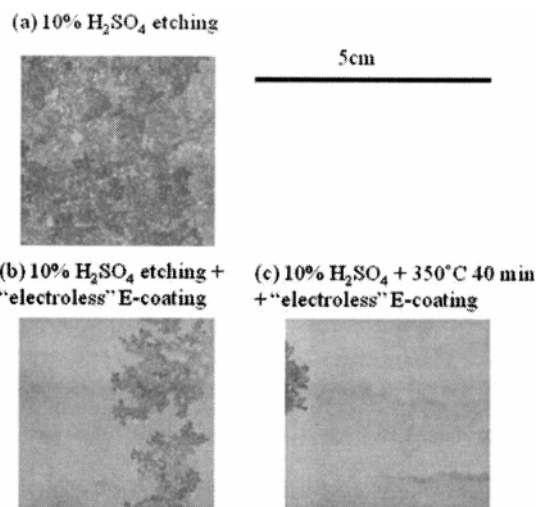


Figure 11. The corrosion damage of acid etched AZ31 samples before and after 24 hour immersion in 5 wt.% NaCl solution.

The results suggest that acid cleaning is also suitable for pre-treating a Mg alloy before “electroless” E-coating. Compared with abrading/polishing, this is a practical process in industries.

Phosphating is a commercial surface treatment technique for many metals. It produces a layer of phosphates on the substrate surface, which has a beneficial contribution to the adhesion of a coating on its top. If a Mg alloy is phosphated, the “electroless” E-coating can still be applied on its surface.

It has been found that the coating on such a treated Mg alloy can remarkably enhance the corrosion resistance of the phosphate surface. Fig.12 shows that on a phosphated AZ91D surface, the right half surface has been “electroless” E-coated; after 2 days of immersion in 5 wt.% NaCl solution, the phosphated and “electroless” E-coated area is uncorroded, while the whole phosphated area without “electroless” E-coating has been very badly corroded.

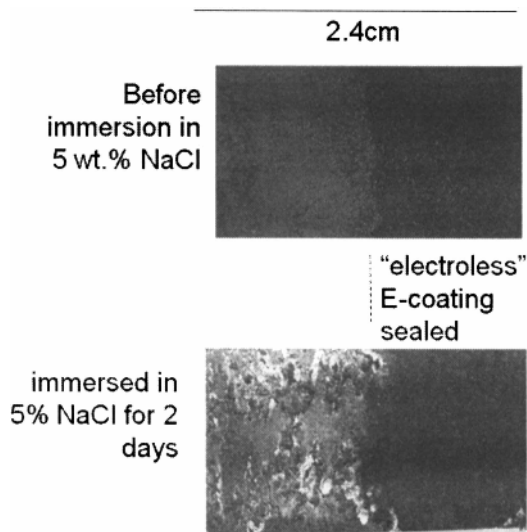


Figure 12. Corrosion morphology of phosphated AZ91D with and without "electroless" E-coating before and after 2 days of immersion in 5 wt.% NaCl solution.

Summary

- 1) An E-coating pre-film can be rapidly self-deposited on a Mg alloy by dipping the Mg alloy in a cathodic E-coating bath solution without applying current or voltage. Such an "electroless" E-coating deposition is a result of Mg surface alkalization effect.
- 2) The "electroless" E-coating is formed only on Mg alloys which have a strong surface alkalization effect. On other metals, such as steel, aluminum and zinc and their alloys, the self-deposited "electroless" E-coating cannot be formed.
- 3) The "electroless" E-coating is thinner than a conventional E-coating. It contains pores which could be the sites to initiate corrosion.
- 4) The pre-film formed on a Mg alloy during "electroless" E-coating process provides adequate corrosion protection for Mg alloys in 5 wt% NaCl solution. Curing can lead to polymerization of the pre-film and significantly enhanced protection performance of the "electroless" E-coating. The discontinuity of the pore liquid in the pores of the coating is responsible for the high corrosion resistance of a coated Mg alloy.
- 5) The protection performance of the coating is closely dependent on the corrosion resistance of the substrate Mg alloy due to the coating porosity nature.
- 6) The substrate surface state and condition can influence the pre-film formation and thus the coating quality. A cleaned and heated Mg alloy surface is most suitable for "electroless" E-coating.
- 7) The "electroless" E-coating process can also be applied on a phosphated Mg alloy surface. The coating can significantly improve the corrosion resistance of a phosphated Mg alloy.

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References

1. J. Gray, B. Luan, "Protective coatings on magnesium and its alloys—a critical review," *Journal of Alloys and Compounds*, 336 (2002), 88-113
2. C. Blawert, W. Dietzel, E. Ghali, G-L. Song, "Anodizing Treatments for Magnesium Alloys and Their Effect on Corrosion Resistance in Various Environments," *Advanced Engineering Materials*, 8 (2006), 511-533
3. G-L. Song, "Electroless E-Coating: An Innovative Surface Treatment for Magnesium Alloys," *Electrochemical and Solid-State Letters*, 12(10) (2009), D77-D79
4. G-L. Song, "Electroless deposition of a pre-film of electrophoresis coating and its corrosion resistance on a Mg alloy," *Electrochimica Acta*, 55 (2010), 2258–2268
5. F. Beck, "Fundamental aspects of electrodeposition of paint," *Progress in Organic Coatings*, 4 (1976), 1-10
6. N. Vatisstas, "Initial Mechanisms of the Electrocoating Process," *Industrial & Engineering Chemistry Research*, 37 (1998), 944-951
7. E. Okada, H. Hosono, T. Nito, et al., "Development of High Throw power E-coat", 2005 SAE World Congress, Detroit, SAE Technical Paper #2005-01-0619 (2005)
8. N. Sato, "Interfacial control between phosphate films and electrodeposition films on coated steels", SAE technical paper #900838, International Congress and Exposition, Detroit, MI (1990)
9. G.-L. Song, "A dipping E-coating for Mg alloys," *Progress in Organic Coating*, 70 (2011), 252-258
10. G.-L. Song, "The Effect of Mg Alloy Substrate on "Electroless" E-Coating Performance," *Corrosion Science*, 53 (2011), 3500-3508
11. G.-L. Song, "Effect of microstructure evolution on corrosion of different crystal surfaces of AZ31 Mg alloy in a chloride containing solution," *Corrosion Science*, 54 (2012), 97-105.