Magnesium: Engineering the Surface

X. B. CHEN,¹ H. Y. YANG,^{1,2} T. B. ABBOTT,^{1,3} M. A. EASTON,¹
and N. BIRBILIS^{1,4}

1.—CAST Co-operative Research Centre and the Department of Materials Engineering, Monash University, Clayton, VIC 3800, Australia. 2.—National Engineering Research Center of Light Alloy Net Forming and State Key Laboratory of Metal Matrix Composites, Shanghai Jiaotong University, Shanghai, People's Republic of China. 3.—Advanced Magnesium Technologies, Sydney, NSW, Australia. 4.—e-mail: nick.birbilis@monash.edu

Magnesium (Mg) and its alloys provide numerous benefits as lightweight materials; however, industrial deployment of Mg in most instances requires anticorrosion coatings. Engineering the Mg surface is an area that has been undergoing intense research recently. Surface engineering commences with the “pretreatment” step, which can be used to modify the surface composition and morphology, resulting in surface enrichment or depletion of alloying elements. Following this, electrochemical plating (including electro- and electroless plating) and conversion coatings have emerged as common means of coating Mg. In this study, we present the key aspects relating to the science and technology associated with pretreatment, electrochemical plating, and conversion coatings. This is followed by experimental examples of engineered surfaces of industrial relevance.

INTRODUCTION

Magnesium (Mg) and its alloys are highly susceptible to aqueous corrosion in near-neutral conditions. Upon atmospheric exposure, Mg rapidly develops porous, poorly bonded, and inhomogeneous oxide/hydroxide/carbonate films¹ which do not provide satisfactory corrosion protection. As such, surface modification and/or surface coatings are necessarily applied upon Mg alloys,² being an effective means to improve corrosion resistance and isolate the base material from the environment. Electrochemical plating³ and chemical conversion coating⁴ are two typical, comparatively low-cost, and easily implemented methods that have been widely adopted in industrial processes. In this paper, we briefly review these two technologies, follow the review with a discussion of the role of coating pretreatment, and then present some experimental results.

ELECTROCHEMICAL PLATING

Electrochemical plating can produce metallic coatings with solderability, electrical conductivity, and decorative appearance, in addition to corrosion and wear resistance. Such coatings are nominally

subdivided into two groups: electroplating and electroless plating. Electroplating (often termed electrodeposition) is a plating process that employs an electrical signal provided by an external power source to reduce cations of a desired metal in solution and produce a metallic coating. Electroless plating is a “self-reduction” process, relying on a process of autocatalytic reduction of metal ions in aqueous solution containing a chemical reducing agent (typically sodium hypophosphite, NaH_2PO_2). At present, electroless Ni-P plating coating is the main electroless process. As the name implies, no external power source is required. Electroplating can yield a thicker and more compact metal coating compared with electroless plating. The pros and cons of these methods are: thinner electroless coatings may have micro-pinholes, which must be subsequently sealed; however, uneven current distribution during electroplating is a challenge for coating components with complex shapes (while electroless plating is a good solution to this). Depending on the service conditions and shape of the components, these two plating methods can be applied separately or in combination to Mg alloys. In fact, a hallmark more typical of coating Mg than any other system is that the final coated products have usually undergone several coating steps (i.e.,

have multilayered coatings). Conventionally, multilayered metal coatings such as Cu/Ni/Cr are deposited on preplated Mg samples for outdoor use, e.g., automotive applications. Noble metals such as Ni/Au multilayers on Mg have been explored for aerospace applications.² Electroless Ni-P coating after sealing is mainly used in mildly aggressive conditions, such as in the computer and electronic (3C) industries.

CONVERSION COATING

In the conversion coating process, the substrate to be protected is immersed in a solution that reacts with the surface, altering the metal ion concentration and the pH at the metal-solution interface.⁵⁻⁷ This process relies on “corrosion” of the substrate to produce metal ions, where the localized change in composition causes precipitation from the solution onto the surface of the substrate to form the coating.⁵⁻⁷ The composition of the base Mg alloy, the pretreatment processes, the composition of the conversion formulations, posttreatments, and operational parameters, such as temperature, pH,⁸ immersion duration, and degree of agitation,⁶ can all influence the structure, composition, and anti-corrosion performance of conversion coatings. A uniform coating with defect-free features is desirable to fulfill its protective role.

Conventional chromate (Cr^{6+}) conversion coatings, though recognized as an effective means of protecting reactive metals (including Mg), have now been banned in many countries due to pollution and safety concerns.^{2,4} Numerous efforts have been made to invent a conversion coating comparable in performance to or better than chromate, such as phosphate/phosphate-manganese,^{9,10} stannate,¹¹⁻¹³ fluoride,¹⁴ rare earth (RE),¹⁵⁻¹⁷ hydrotalcite,⁷ ionic liquid,¹⁸ molten salt,¹⁹ vanadium,²⁰ stearic acid,²¹ *etc.*, but each case has its own disadvantages. Stannate, RE, ionic liquid, and molten salt conversion coatings are not applicable for practical use at this stage, due to either the high cost of raw materials or long coating duration; fluoride and vanadium-based coatings still have toxicity issues, and stearic acid coatings require high operational temperatures. Calcium phosphate conversion coatings are noteworthy for their simplicity in operation, low cost, and low environmental impact.^{2,4} In existing reports,⁶ the formation of calcium phosphate coatings led to an improvement in corrosion resistance relative to untreated alloy, revealing a promising candidate for good corrosion resistance.

PRETREATMENT

In regards to Mg coatings, there is a requirement that they must be uniform, adherent, and pore-free, otherwise rapid corrosion occurs due to loss of the barrier effect (it being prudent at this point to emphasize that Mg coatings provide a barrier effect, and not active anodic protection, such as

galvanizing does to steel, since no practical anodic coatings for Mg exist owing to Mg being so reactive itself).²⁻⁴ To achieve this, one of the most difficult and critical aspects is to develop an appropriate pretreatment process; this is the necessary precursor to all coating steps and hence requires special attention with regards to engineering the surface. Once a suitably presented alloy surface can be realized, many desired coatings can be readily achieved.² It is not trivial to plate protective coatings onto Mg alloys. Because of the low solubility of most metals in Mg (but the requirement of alloying to achieve strength), an electrochemically heterogeneous surface of alloy surfaces exists (for example, such as for AZ91D, Fig. 1), such that each component behaves differently in the plating bath, leading to nonuniform coating growth. Consequently, pretreatment is a key step to coating Mg, mainly including the following steps in no specific order: mechanical pretreatment, acid activation/pickling, and alkaline cleaning/conditioning.

Regarding electro- and electroless plating techniques, undercoating is also essential prior to plating, to improve adhesion and reduce galvanic corrosion between metal coatings and the Mg substrate.²²⁻²⁴ So far, two types of undercoatings: Zn immersion followed by pre-electroplating (Cu, Zn or Ni or Ni/Cu or Zn/Cu) and Ni by electroless plating, are used for subsequent electroplating.² Once a suitable undercoating is successfully plated on substrates of Mg alloys, many other metals with desired properties can be electrodeposited (we present a relevant example below).

Using AZ91D as the principal example, the typical conversion coating process is as simple as immersion in appropriate chemicals, and can be preceded by any number of pretreatment steps to aid in optimization of the coating (final step). Pretreatments must necessarily impart some sort of functionality by modification of the alloy surface. The microstructural impact (phenomenologically) of

Fig. 1. Backscattered electron micrograph of AZ91D (as polished) revealing two-phase structure.

Fig. 2. Schematic representation of AZ91D surface (in section view) following the various pretreatment processes: (a) as polished, (b) activator treated, (c) conditioner treated, and (d) activator + conditioner treated.

the most common pretreatment procedures is shown in Fig. 2 for AZ91D. “Activator” pretreatment (the common term given to acid treatment) is shown to attack the Mg matrix but leave the β -phase essentially unaffected. In the case of “conditioner” pretreatment (the common term given to alkaline treatment), the opposite is true, whereby β -phase is preferentially removed (since the Al-containing phase dissolves at high pH, whereas the matrix is essentially unaffected, since Mg is passive in alkaline conditions).²⁵ As a result, the careful selection, or even combination of, activator and conditioner treatments allows one to clean, degrease, functionalize, and homogenize the surface of an alloy prior to ultimate coating.

EXPERIMENTAL PROCEDURES

Material Preparation and Coatings

In this work, samples of AZ91D [Mg-9.02Al-0.49Zn, wt.% as measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES)] from alloy supplier HNKWE (Henan Province, China) were used. A Toshiba 250-ton clamping force cold chamber high-pressure die casting (HPDC) machine was used to cast test plates of 70 mm $\times$ 60 mm $\times$ 2 mm in size. SiC paper (1200 grit) was used to remove traces of die spray and the as-cast surface layers from samples.

For coatings, rather than present the whole range of chemicals used in pretreatment and coatings here, the details are presented with the relevant information in the relevant sections. Generally, however, pretreatment was executed prior to conversion coating, electroless plating, or Zn immersion (which is a post-pretreatment step and precursor to electrodeposited coatings). Electrodeposition of Zn was further performed on Zn-immersion-treated AZ91D. In cases where electroplating was performed, the rear of specimens was drilled and tapped so that a wire for electrical connection could be

attached, and specimens were then mounted with an appropriate resin, exposing a free surface to be electroplated.

Characterization

Electrochemical tests were conducted using a flat cell (PAR) with electrode area of 1 cm². The reference electrode used was a saturated calomel electrode (SCE), and the counterelectrode was Ti mesh. A Biologic® VMP-3Z potentiostat was used to execute potentiodynamic polarization measurements at sweep rate of 1 mV/s. Scanning electron microscopy (SEM) was carried out using an FEI Nova Nano and Jeol 7001F.

EXPERIMENTAL EXAMPLES OF COATING SYSTEMS

It is not possible, in one manuscript, to give a holistic description and demonstration of the range of coatings available. Therefore, some selected examples are given to emphasize the function and importance of pretreatments, electrochemical coatings, and conversion coatings.

Conversion Coatings

Pretreatment is a critical step in the development of suitably performing coatings, and was recently shown to be as important, if not more important, than the final coating itself.^{2,4} Pretreatments in the case of conversion coatings can serve several purposes, but are principally used to homogenize the surface in order to minimize local galvanic cell activity. The classic example is pretreatment of AZ91D as depicted in Fig. 3. What is seen is that, following activation [in 10 g/L sodium nitrate (NaNO₃) and 1 mL/L phosphoric acid (H₃PO₄) solution at room temperature for 2 min], surface roughness increases dramatically and the apparent density of β -phase is increased owing to surface recession of the α -matrix. The extent to which this

Fig. 3. Backscattered electron micrographs of AZ91D following activation and conditioning as compared with the as-ground condition.

occurs can be regulated by the selection of temperature, time, and chemistry/pH of the activator bath. Conversely, following conditioning [in 200 g/L sodium hydroxide (NaOH) at 70°C for 5 min], we can observe (Fig. 3) selective dissolution of β -phase, leaving cavities. The combination of activation and conditioning is effective to remove the β -phase. We emphasize that failure to homogenize and pretreat the surface renders the subsequent conversion coating defective (and hence ineffective) owing to failure to coat β -phase particles, since the chemical conversion process is restricted to sites of high metal ion activity such as the α -matrix.

Regarding conversion coatings for AZ91D, recent focus has been on calcium phosphate coatings, which have shown appreciable corrosion resistance^{5, 26} owing to the formation of the $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ compound on the surface, and also the possibility to be posttreated to stimulate precipitation of hydroxyapatite [$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$].⁵ The latter displays good chemical stability and inertness in neutral/service conditions.

The final conversion coating (following the aforementioned activation and conditioning) is 2.36 g/L $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 0.82 g/L Na_3PO_4 . Ca^{2+} ions were added in the form of calcium nitrate tetrahydrate, and sodium phosphate was used as source of PO_4^{3-} ions. The pH of the coating solutions was adjusted to

Fig. 4. Potentiodynamic polarization curves in 0.1 M NaCl for AZ91D and AZ91D + activator, conditioner, and calcium phosphate conversion coating. Inset: backscattered electron micrograph of conversion-coated specimen.

pH 3.0 using nitric acid (HNO_3) with conversion coating carried out at 40°C for 5 min. Digital temperature controllers were used to maintain the bath temperature. We observe from Fig. 4 that the calcium phosphate coating (SEM image inset, showing

the coating presence and subsequent dehydration cracking under vacuum conditions) gives a significant shift in the anodic reaction kinetics on AZ91, and as such can reduce the corrosion rate whilst ennobling the potential.

ELECTROCHEMICAL COATINGS

In the case of electrochemical coatings, again, pretreatment is crucial prior to plating.² Herein, we show the effect of pretreatment on the two main types of undercoatings for subsequent electroplating: (1) electroless Ni, and (2) Zn immersion followed by pre-electroplating (again Zn). To avoid confusing readers who may be new to Mg coatings, we emphasize that final electroplated coatings on Mg are not produced directly upon Mg alloy surfaces. This is because the Mg surface itself is not suitable for electrodeposition of most metals, since it is not capable of sustaining reduction reactions, viz. coating deposition, at sufficient rates.

Typically, following chemical pretreatment, preplating is also executed, the most common being Zn immersion to form a Zn-rich layer on the Mg surface, and then preplating Cu to form a Cu-rich

layer on the Zn layer (also enhancing the reduction reaction rate upon the surface for final electrodeposition). Nowadays, however, preplating Zn is intensively studied as a green alternative to preplating Cu (from cyanide-containing baths).

Historically, chromium compounds and fluoride have been used as pickling pretreatment of Mg alloys prior to commencement of electroplating steps. As such, we present some results comparing this process (which is progressively being restricted due to toxicity) as compared with a more environmentally friendly pretreatment. Following alkaline degreasing/conditioning (60 g/L NaOH + 10 g/L Na₃PO₄·12H₂O, 80°C, 10 min), AZ91D was immersed in a HNO₃ + CrO₃ pickling solution and HF activated (125 g/L CrO₃ + 110 mL/L HNO₃, room temperature, 30 s; 385 mL/L 40% HF, room temperature, 8 min), producing the surface shown in Fig. 5a. This treatment partially dissolves the matrix and preferentially etches the boundary between α and β phase, resulting in high surface roughness. In contrast, following conditioning and pickling (30 g/L 85% H₃PO₄ + 100 g/L Na₃PO₄·12H₂O + 20 g/L KMnO₄, room temperature, 5 min), the surface is relatively smooth and it is impossible to clearly distinguish the α and β phases

Fig. 5. Backscattered electron micrographs showing surfaces following: (a) CrO₃ + HNO₃ pretreatment, (b) H₃PO₄ pretreatment, (c) treatment as in (a) followed by electroless Ni-P coating, and (d) treatment as in (b) followed by electroless Ni-P coating (full chemical details given in text).

(Fig. 5b). The prevalence and characterization of very thin films on the surface that result from pickling are not described herein for the sake of brevity; however, their existence has already been documented.²⁷

Following the above pretreatments, electroless Ni-P plating (15 g/L $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 4.8 g/L $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, 22 g/L $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, 8.5 g/L NH_4HF , 9 mL/L 40% HF, pH adjusted to 6 by NH_4OH , 80°C, 30 min) was applied to the specimens (Fig. 5c, d). The purpose of this comparison is to reveal that, depending on the pretreatment applied, the Ni-P

morphology will differ significantly. Electroless Ni-P coating on AZ91D pretreated by the H_3PO_4 process shows a more uniform and dense surface film which could also be used as a good undercoating for subsequent plating. This example also shows that the scope and number of potential pretreatments are large, and indeed semi-infinite, making pretreatment optimization an area of vigorous present and future research.

To give a different example related to Zn immersion, the role of two different pretreatments is again presented. Zn immersion was performed in 50 g/L $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ + 150 g/L $\text{K}_2\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ + 7 g/L $\text{KF} \cdot 2\text{H}_2\text{O}$ + 6 g/L Na_2CO_3 (80°C, 5 min). The specimens immersed were AZ91D that was conditioned and pickled in 30 g/L 85% H_3PO_4 + 100 g/L $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ + 20 g/L KMnO_4 (room temperature, 5 min) and also AZ91D pretreated in 200 mL/L 85% H_3PO_4 + 1 g/L $\text{Na}_2\text{Mo}_4 \cdot 2\text{H}_2\text{O}$ (45°C, 15 s), 80 g/L $\text{Na}_4\text{P}_2\text{O}_7$, 20 g/L Na_2CO_3 , 30 g/L NaNO_3 (80°C, 10 min), and 385 mL/L 40% HF (room temperature, 8 min). The whole surface of AZ91D treated by either of the above processes was covered by a Zn immersion film (Fig. 6). However, a much more compact Zn immersion film was formed on AZ91D after being treated by the H_3PO_4 process (Fig. 6, top), again showing the key role of pretreatment.

To take an example through to completion in the case of electrodeposited coatings, the specimen from Fig. 6 (top) was electrodeposited with a zinc coating. Electrodeposition of Zn (which was itself the counterelectrode material) was performed in 10 g/L ZnO + 120 g/L KOH + 20 g/L KF (room temperature, 30 min, 80 mA/cm²). A metallic Zn coating can be plated very well on AZ91D, provided the critical pretreatment and undercoating have been executed, as shown in Fig. 7. The Zn coating consists of nanoparticles with size ~25 nm. The cross-section shows that the Zn coating is compact and homogeneous over the substrate.

Figure 8 presents the potentiodynamic polarization response of AZ91D, AZ91D with a Zn immersion film, and AZ91D with electrodeplated Zn (above a zinc

Fig. 6. Morphology of surface of AZ91D following Zn immersion for a (top) H_3PO_4 pretreated sample, and (bottom) H_3PO_4 + Na_2Mo_4 (+HF-activated) pretreated sample.

Fig. 7. Left: view from above of the surface of Zn-electrodeposited AZ91D pretreated, then Zn-immersion treated; right: cross-sectional view of specimen on left, where the uniform and defect-free nature of the coating is evident.

Fig. 8. Potentiodynamic polarization curves in 0.1 M NaCl for AZ91D, AZ91D following Zn immersion (which followed the H_3PO_4 pretreatment), and AZ91D following Zn immersion and Zn electrodeposition.

immersion film) for the specimen in Fig. 7. Following Zn immersion, the corrosion potential is ennobled; however, the corrosion rate is enhanced (owing in part to the enhanced cathodic activity of Zn), indicating that the Zn-immersion film is not an effective protective coating for the substrate. Following electrodeposition, the corrosion potential is further ennobled and the corrosion rate decreased after electrodeposition of the Zn coating, since the complete Zn coverage retards anodic dissolution and renders the sample behavior to be that of Zn and not Mg.

CONCLUSIONS

Herein, the key aspects relating to the science and technology associated with pretreatments, electrochemical plating, and conversion coatings are described, albeit in a quick overview manner, followed by examples of engineered surfaces of industrial relevance. The chemical composition of the conversion coating/plating bath plays a critical role in their anticorrosion performance; however, it was shown that the coating performance also heavily relies on appropriate pretreatments to functionalize the surface. Developing better, simpler, cheaper, and environmentally friendly coating technologies is and will remain a hot topic needing further investigation, likely to be fuelled by the advantages of the weight reduction that Mg can provide when fully exploited in practical applications.

ACKNOWLEDGEMENTS

The CAST CRC was established under, and is funded in part by, the Australian Commonwealth Government Cooperative Research Centre scheme. H.Y.Y. and N.B. thank the CSC Scheme (China).

REFERENCES

1. M. Santamaria, F.D. Quarto, S. Zanna, and P. Marcus, *Electrochim. Acta* 53, 1314 (2007).
2. J.E. Gray and B. Luan, *J. Alloy. Compd.* 336, 88 (2002).
3. X.-B. Chen, H.-Y. Yang, T.B. Abbott, M.A. Easton, and N. Birbilis, *Corrosion* 68, 518 (2012).
4. X.-B. Chen, N. Birbilis, and T.B. Abbott, *Corrosion* 67, 035005 (2011).
5. X.-B. Chen, T. Abbott, and N. Birbilis, *Corros. Sci.* 53, 2263 (2011).
6. Y. Song, D. Shan, R. Chen, F. Zhang, and E.-H. Han, *Corros. Sci.* 51, 62 (2009).
7. J.K. Lin and J.Y. Uan, *Corros. Sci.* 51, 1181 (2009).
8. C.S. Lin, H.C. Lin, K.M. Lin, and W.C. Lai, *Corros. Sci.* 48, 93 (2006).
9. Y. Song, D. Shan, R. Chen, F. Zhang, and E.-H. Han, *Surf. Coat. Technol.* 203, 1107 (2009).
10. W.Q. Zhou, D.Y. Shan, E.H. Han, and W. Ke. Preparation Method of Magnesium Alloy Chromeless Chemical Conversion Film and its Used Film Forming Solution. CN1475602A, 02-18, 2004.
11. H. Huo, Y. Li, and F. Wang, *Corros. Sci.* 46, 1467 (2004).
12. H.H. Elsentriecy, K. Azumi, and H. Konno, *Electrochim. Acta* 53, 4267 (2008).
13. F. Zucchi, A. Frignani, V. Grassi, G. TrabANELLI, and C. Monticelli, *Corros. Sci.* 49, 4542 (2007).
14. K.Y. Chiu, M.H. Wong, F.T. Cheng, and H.C. Man, *Surf. Coat. Technol.* 202, 590 (2007).
15. H. Ardelean, I. Frateur, and P. Marcus, *Corros. Sci.* 50, 1907 (2008).
16. C. Wang, S.L. Zhu, F. Jiang, and F.H. Wang, *Corros. Sci.* 51, 2916 (2009).
17. M.F. Montemor, A.M. Simões, and M.J. Carmezim, *Appl. Surf. Sci.* 253, 6922 (2007).
18. N. Birbilis, P.C. Howlett, D.R. MacFarlane, and M. Forsyth, *Surf. Coat. Technol.* 201, 4496 (2007).
19. M.F. He, L. Liu, Y.T. Wu, Z.X. Tang, and W.B. Hu, *Corros. Sci.* 50, 3267 (2008).
20. K.H. Yang, M.D. Ger, W.H. Hwu, Y. Sung, and Y.C. Liu, *Mater. Chem. Phys.* 101, 480 (2007).
21. X.P. Lei, G. Yu, Y.P. Zhu, Z.P. Zhang, X.M. He, B.N. Hu, and Y. Chen, *Trans. Inst. Metal Finishing* 88, 75 (2010).
22. J.-W. Tang and K. Azumi, *Surf. Coat. Technol.* 205, 3050 (2011).
23. Y.-F. Jiang, C.-Q. Zhai, L.-F. Liu, Y.-P. Zhu, and W.-J. Ding, *Surf. Coat. Technol.* 191, 393 (2005).
24. C.-D. Gu, J.-S. Lian, J.-G. He, Z.-H. Jiang, and Q. Jiang, *Surf. Coat. Technol.* 200, 5413 (2006).
25. M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, 2nd ed. (Houston, TX: National Association of Corrosion Engineers (NACE), 1974).
26. X.-B. Chen, T. Abbott, and N. Birbilis, *Corros. Sci.* 55, 226 (2012).
27. H.-Y. Yang, X.-B. Chen, X.W. Guo, G.H. Wu, W.J. Ding, and N. Birbilis, *Appl. Surf. Sci.* 258, 5472 (2012).