Growth Behavior of Initial Product Layer Formed on Mg Alloy Surface Induced by Polyaniline

Yizhong Luo,a,b,∗ Xianhong Wang,a,∗ Wei Guo,a and Michael Rohwerdera,b,∗,∗

a Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People’s Republic of China
b Max-Planck-Institut für Eisenforschung GmbH, 40237 Düsseldorf, Germany

The quality of the interfacial protective layer induced by polyaniline (PANI) has been claimed to play a crucial role for the enhanced corrosion protection of Mg alloy, but its growth behavior is not well understood. Here some composition, structure and growth kinetics of the protective layer formed at the PANI-emeraldine base (EB) coating/AZ91D Mg alloy interface were investigated to explore the growth mechanism. Upon immersion in 0.5 M NaCl solution, the growing interface layer under EB coating exhibited a fast passivation rate and an increased corrosion resistance, which was largely influenced by ion concentration. XPS depth profiles showed that the EB-induced layer was a mixture of MgO and Mg(OH)2, in which no significant bi-layer structure existed and MgO was dominant throughout the bulk film. These observations suggest that the interaction between EB and Mg can promote the faster growth of a stable MgO-rich layer mixed with Mg(OH)2 probably by solid reaction. Meanwhile less hydration of MgO and dissolution-precipitation reaction occur, thus leading to less Mg(OH)2 in the outer layer.

© The Author(s) 2015. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.1101506jes] All rights reserved.

Manuscript submitted January 2, 2015; revised manuscript received March 9, 2015. Published March 23, 2015.

Magnesium alloys have drawn great attention in automotive and aerospace industry due to their excellent properties such as low density and high specific strength. However, limited corrosion resistance of such alloys has retarded their widespread applications. To improve the corrosion resistance of Mg alloys, numerous coating techniques have been explored, among which organic coating containing corrosion inhibiting pigments is an economical and effective method in industry. One important pigment for Mg alloys is polyaniline (PANI) including emeraldine salt form (ES) and emeraldine base form (EB).1–6 Its highly efficient corrosion-protection performance for Mg alloys has been shown to be competitive to a chromate-pigmented coating.7 Additionally, self-healing capability was also found on a hybrid sol-gel/PANI coated Mg alloy upon immersing in Harrison’s solution, where no pitting or filiform corrosion occurred around the scratched area while a protective layer was formed.3 Sathiyanarayanan et al.1 and Wang et al.3 observed that, after an initial decrease upon immersion in corrosive electrolytes, the complex impedance of PANI coated Mg alloy recovered, which was attributed to the formation of a protective layer. The different chemical composition on the EB-induced protective layer surface was already confirmed by X-ray photoelectron spectroscopy (XPS) in comparison with that formed underneath a varnish coating.2,6

The mechanism of PANI promoting a protective layer formation has been mostly supported by extensive studies in various metal systems.9–14 Nevertheless, few works have been done to understand the protective layer growth behavior. The most intractable issue of how the interaction between PANI and metal induces the protective layer growth still remains unsolved.9 This is attributed primarily to the great difficulty in in-situ investigation on the growth kinetics of interfacial layer formed beneath a coating. Electrochemical polarization methods as well as surface analysis techniques are usually employed to study the anodic film formation on bare metal surface.15–18 but are inappropriate to characterize the buried interface. Up to now, few studies have been carried out to clarify the growth kinetics of the protective layer, let alone unveil the effect of PANI on the film growth.

Recently, open circuit potential (OCP) measurement was applied to characterize the initial growth kinetics of interfacial oxide layer in situ, as it is quite sensitive to the electrochemical change of electrode surface, even the interfacial reactivity under coatings. Burstein et al. found that the corrosion potential of freshly generated aluminum increased linearly with the logarithm of immersion time during repassivation, which was interpreted to be correlated to the oxide film growth.19–24 This relationship between OCP and immersion time has been utilized to study the growth kinetics of oxide film formed on the bare metal surface25–31 as well as at the coating/metal interface.32

Therefore, in this work the OCP method in combination with XPS and electrochemical impedance spectroscopy (EIS) techniques was applied to comprehensively explore the growth behavior of the EB-induced protective layer and to find out the difference to the growth process occurring without EB. This study is the first attempt to formulate a possible growth mechanism of EB-induced product film on Mg alloy.

Experimental

All AZ91D Mg alloy panels were purchased from Yinhe Magnesium Alloy Co. LTD, China (Composition in wt%: Al, 8.9; Zn, 0.7; Mn, 0.37; Fe, ≤0.005; Si, ≤0.01; Be, ≤0.02; Cu, ≤0.03; Mg, bal. which was determined by Energy Dispersive X-ray Fluorescence (ED XRF) and is provided by provider). Square samples (20 mm × 20 mm × 2 mm) were manually dry ground with silicon carbide paper up to a 1000 grit surface, ultrasonically degreased in acetone and then dried in air. The preparation of EB layer was described in previous work.6 The EB film coated Mg alloy was made by applying EB/N-methyl-2-pyrrolidone solution (1 wt%) on alloy surface and dried under infrared light based on the earlier work.32 After exposure of EB-coated Mg alloy in electrolyte, the EB film was removed by using adhesive tape. The polynonyl butyral (PVB) coated Mg alloy was prepared by spin coating 10 wt% PVB/ethanol solution on metal surface. Each test sample was sealed by epoxy resin with exposed working area of 1 cm2.

OCP measurement was performed on a Solartron 1287 electrochemical interface, and EIS was employed on an Ivium CompactStat. For corrosion tests in electrolyte, a three-electrode cell was employed consisting of the test sample as the working electrode, a saturated calomel electrode as reference electrode and a platinum sheet as counter electrode. EIS data were obtained at the open circuit potential with 10 mV perturbation in the frequency range of 10−1–107 Hz. XPS measurements were performed on a PHI Quantera II (Physical Electronics, Chanhassen, MN, USA) using a monochromatic Al Kα (1486.7 eV) operating at 15 kV and 25 W. For XPS sputtering, the underlying alloy surface was bombarded with Ar+ ions at a sputter rate of 3.7 nm min−1, based on a SiO2 standard (a thermal oxidized SiO2 film, supplied by PHI). Sputtering was done
Results

Formation and corrosion resistance of product layer.— Fig. 1a shows the OCP evolution of bare Mg alloy and EB coated Mg alloy (EB/Mg alloy) as a function of immersion time in 0.5 M NaCl solution at 25°C. The whole immersion time for the two samples can be divided into three stages: t1-t2, t2-t3, and > t3. In the first stage (t1-t2), an abrupt drop in potential was observed for the bare Mg alloy (more visible in the inset figure), which could be ascribed to an activation of the surface through the degradation of the air-formed oxide layer on the metal surface as well as the anodic dissolution of Mg alloy after immersion in electrolyte. The EB/Mg alloy had a higher initial potential than the bare Mg alloy due to the presence of the EB film. However, the barrier property of the EB film was so poor that the electrolyte could easily penetrate to the interface and react with the substrate surface, leading to a potential decrease during immersion. In the second stage (t2-t3) the increase of OCP might be correlated to the growth of corrosion product layer, which could slow down the anodic dissolution to some extent. XPS depth-profiling (Fig. 2) confirmed that both product layers indeed thickened with immersion time during this period. However, the EB/Mg alloy exhibited a higher terminal potential than the bare Mg alloy, implying that the product layer formed at the EB film/Mg alloy interface possibly possessed a higher corrosion resistance than that generated on the bare Mg alloy surface.

After the OCP measurements, EIS was carried out for the bare Mg alloy and also for the EB/Mg alloy after removal of the EB film. As depicted in Fig. 1b, the Nyquist plots reveal a capacitive loop at the high frequency region corresponding to the charge transfer reaction, and an inductive loop at the low frequency region related to the relaxation of adsorbed species or the concentration of Mg ions on relatively film-free area. In general, the diameter of the capacitive loop is associated with the charge transfer resistance. The larger the diameter, the higher the corrosion resistance of electrode. EB/Mg alloy had a diameter of 1100 Ω cm², which was twice larger than that of 640 Ω cm² for bare Mg alloy, again indicating an improved protective layer was formed under the EB coating. Therefore, it is concluded that EB makes the product layer formed at the EB/Mg alloy interface different from the naturally generated one. Now the unsolved issue is how the EB influences the growth behavior of such a product film to make the differences, which will be discussed below.

XPS study of composition and structure of product layer.— For a better understanding of the product layer growth, the film composition and structure are important prerequisites. Fig. 3 shows the XPS depth profiling spectra of Mg 2s and O 1s of the corrosion product layer naturally generated on bare Mg alloy surface after 100 second immersion at OCP in 0.5 M NaCl solution. At the beginning of sputtering, the Mg 2s XPS spectra (Fig. 3a) primarily exhibited two components: MgO (at 89 ± 0.1 eV) and Mg(OH)2 (at 87.1 ± 0.2 eV), perhaps some MgCO3 as well at the top surface. As the sputtering time increased, the intensity of the Mg(OH)2 peak decreased gradually whereas the MgO peak was enhanced, meanwhile another new peak at 88.1 ± 0.1 eV appeared and became stronger corresponding to the metallic Mg.
Figure 3. XPS depth profiling spectra of Mg 2s (a) and O 1s (b) of the oxide layer naturally generated on bare Mg alloy surface after 100 second immersion at OCP in 0.5 M NaCl solution. The estimated sputtering rate is approximately 3.7 nm per minute based on a SiO2 standard.

Figure 4. Evolution of Mg(OH)2, MgO and metallic Mg peak area ratio obtained in Mg 2s XPS spectra (a), O2− and OH− peak area ratio as well as the ratio of O2−/OH− obtained in O 1s XPS spectra (b) with sputtering time for the natural product layer on bare Mg alloy surface.
Figure 5. XPS depth profiling spectra of Mg 2s (a) and O 1s (b) of the oxide layer formed at the EB film/Mg alloy interface obtained after 1000 second immersion at OCP in 0.5 M NaCl solution. The estimated sputtering rate is approximately 3.7 nm per minute based on a SiO2 standard.

MgO and Mg curves as well as that of the Mg(OH)2 and Mg curves both moved to the right direction, indicating an increase in thickness of the interfacial product layer after 500 s immersion. Comparing the three EB-induced layers of 100 s, 500 s and 1000 s immersion, it could be found that the amount of MgO and Mg(OH)2 both increased in the newly formed film, but the MgO content was always higher than the Mg(OH)2 one. Contrarily, the new corrosion product layer formed on bare Mg alloy after 100 s immersion, which had a similar thickness as the EB-induced film of 1000 s immersion, was dominated by Mg(OH)2 with some MgO (Fig. 4). Hence, it is reasonable to assume that EB can enhance the MgO information or/and retard the production of Mg(OH)2.

EIS study of impedance evolution of product layer.— EIS was also used for studying the formation of the corrosion product layer on bare Mg alloy and EB-coated samples. EIS spectra obtained during the first 30 min immersion in 0.5 M NaCl solution are shown in Fig. 8. For the EB/Mg alloy, since the electrolyte had not yet reached the substrate surface, only one time constant was seen at the high frequency in the first 2.5 minutes (Fig. 8a), which was associated with EB coating. Subsequently, two time constants became apparent with the advent of the second time constant at the middle frequency corresponding to the electrochemical reaction at the coating/substrate interface. With increasing immersion time, the phase angle at high frequency (the insert in Fig. 8a) was found to decrease gradually, indicating the reduced barrier property of EB coating. In the meantime, the phase angle at the middle frequency range increased noticeably. For the coating systems, the variation of phase angle at the middle frequency range with time is usually associated with the evolution of electrode resistance.41 The rapid enhancement of phase angle as well as the remarkably increasing diameter of the semicircle in Nyquist plots (Fig. 8a) within the first 10 min might be indicative of the fast formation of a more protective layer. On the contrary, for the bare Mg alloy the phase angle (the insert in Fig. 8b) and the semicircle diameter (Fig. 8b) almost kept constant at the beginning, indicating that the newly growing film exhibited less capacity for passivity.

OCP measurement for the growth kinetics of product layer.— Recently, open circuit potential (OCP) measurements were applied to characterize the initial growth kinetics of different oxide layer in situ. Burstein et al.19–24 found that the free corrosion potential of freshly generated aluminum surface increased linearly with the logarithm of time during repassivation as the result of oxide film growth. The linear relationship of corrosion potential (E) and log time (t) is suggested to follow Eq. 1:

\[ E = a_1 + b_1 \log t \]
where $a_1$ and $b_1$ are constants. The linearity of OCP with log time has been modelled in terms of the growth kinetics of the oxide layer. A generic model was proposed by Cabrera and Mott\textsuperscript{42} to describe the kinetics of oxide film growth on metal by the transport of cations across the film to film/solution interface under the effect of a high electric field.

Abd El Kader et al.\textsuperscript{43} reported that the relationship of OCP ($E$) of the metal with immersion time ($t$) can be fitted to Eq. 2:

$$E = \text{const.} + 2.303 \left( \frac{\delta^-}{B} \right) \log t$$  \[2\]

where $\delta^-$ is the growth rate of the oxide film per unit decade of time, and $B$ is a constant. In the early reports,\textsuperscript{28–30,32,43} it was demonstrated that the evolution of oxide layer can be detected based on this linear slope, which can reflect the growth kinetics of oxide layer.

The insert of Fig. 1a shows the OCP evolution against logarithmic time for bare and EB-coated Mg alloys. A nearly linear relationship was observed in the second period, which indicated that the growth of both films followed a direct logarithmic law. However, note that the onset of the rise of OCP is different for bare and coated samples, which makes a direct comparison of the OCP-log ($t$) plots questionable. The reason for the delay of the rise of OCP for the EB coated sample is most likely due to the time necessary for electrolyte to permeate the EB coating. Therefore, we compared the EB coated sample with a PVB coated one, where the onset was delayed similarly. Interestingly, the EB/Mg alloy exhibited a higher value of $\frac{\partial E}{\partial \log t}$ than the PVB-coated sample as shown in Fig. 9. For reproducibility, replicate experiments were performed and are listed in Table I.

Based on the aforementioned studies and the above OCP results, it is proposed that the EB-induced protective layer exhibits different growth behavior from the naturally generated one without the influence of EB. Note that the value of $\frac{\partial E}{\partial \log t}$ for EB/Mg alloy was higher than that for bare Mg alloy, while the product layer on the EB/Mg alloy interface thickened slower than that on bare Mg alloy. However, the protective quality of the product layer seemed to grow faster for the EB-induced layer. As presented in Fig. 8, the EIS data show that within the first 10 min of immersion, the phase angle and the semicircle diameter of EB/Mg alloy increased apparently with immersion time, while there was no significant change for those of bare Mg alloy. This finding indicated that a fast formation of a more protective layer occurred at EB/Mg alloy interface, while the faster growing film on bare Mg alloy surface exhibited less capacity for passivity. In addition, the XPS data revealed that the EB-induced protective layer
had a different composition compared with the not EB-induced product layer. Therefore, we consider that the linear slope of OCP-log t curve reflects the passivation rate, i.e. the formation rate of a protective performance, which involves the evolution of chemical and physical structures.

The curves in Fig. 10a–10d represent the variation of open-circuit potential of the EB/Mg alloy with immersion time at 25°C in NaCl solutions of different concentrations, and the plots of OCP against log t time are shown as insets. The OCP of each sample rose at a similar location along the log t axis, but a decrease of linear slope was observed when the NaCl concentration increased from 0.01 M to 0.5 M (Fig. 10e). This is attributed to a competitive process between passivation and dissolution-preparation reaction. In the case of low concentration of Cl−, the growth process of EB-induced protective layer dominates. With further increase of the Cl− anion concentration, the hydration of the protective layer and the dissolution-participation reaction of Mg substrate caused by the aggressive anion are likely to prevail, and thus a porous secondary hydroxide layer forms. Under this circumstance of high ion concentration, the thickness of the corrosion product layer would increase due to severe corrosion, but the passivation ability of the metal surface would decline. Note that the anodic shift of OCP is most likely due to a more prominent suppression of the anodic reaction with oxygen growth than of the cathodic reaction. Therefore, the “passivation rate of oxide layer” that is proposed in this work to elucidate the linear slope of the OCP-log t curve can perfectly explain the experimental observation that the straight linear slope of the OCP-log t curve decreases with the increase of Cl− ion concentration.

**Discussion**

**Corrosion product layer formed without the influence of EB.** — For the corrosion product film on bare Mg alloy, the evolution of O2− and OH− peak area ratio with sputtering time in Mg 2s (Fig. 4a) and O 1s (Fig. 4b) XPS depth profiles illustrated that Mg(OH)2 dominated in the outer layer, while enrichment of MgO was found in the inner layer, indicating an apparent bi-layer structure. Therefore, with depth the ratio of MgO and Mg(OH)2 showed a significant change at the Mg(OH)2-rich outer layer/MgO-rich inner layer interface (Fig. 4).

Based on the excellent works by Taheri et al., a simple physical model showing the growth of the product layer on Mg alloy surface naturally formed after exposure in 0.5 M NaCl solution is shown in Fig. 11a. It is assumed that when bare Mg is exposed to the corrosive electrolyte, the anodic oxidation of Mg to both MgO and Mg2+ takes place first. Aging in water may cause incomplete hydration of MgO to Mg(OH)2. In addition, the precipitation of Mg2+ ions, which have transported through the permeable MgO film and entered the electrolyte, also results in the formation of Mg(OH)2 layer.

\[
\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \quad [3]
\]

\[
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad [4]
\]

\[
\text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2 \quad [5]
\]

As the dissolution-precipitation reaction is dominant during corrosion, a thick porous platelet Mg(OH)2-rich outer layer grows with immersion time (Fig. 11a), which cannot efficiently passivate the Mg alloy surface and thus shows a slow passivation rate and a low corrosion resistance.

**EB-induced protective layer on Mg alloy.** — For the EB-induced film, its chemical structure seemed not to be a distinct bi-layer structure. Although the MgO/Mg(OH)2 ratio also decreased from the Mg/film interface to the film/electrolyte interface in Mg 2s depth profiles, the decrease rate was slower than that for bare Mg alloy and no significant sudden change occurred inside the film (Fig. 6a). In addition, more MgO content was observed in the sub-layer of the EB-induced film (Fig. 6a) compared with the natural corrosion product film (Fig. 4a), indicating less formation of Mg(OH)2-rich outer layer during immersion.

Note that Al exists in the AZ91D Mg alloy, and it may affect the corrosion behavior by formation of Al2O3 or Al(OH)3, incorporated into the surface film during corrosion. Al XPS depth profiling spectra indeed showed a small amount of Al in both product layers for the bare Mg alloy and the EB-coated one. However, these Al peaks were very weak, and no significant differences were found for the Al contents between the two surface films. Hence, it is assumed that Al does not play a role here.

A comparison of OCP linear slopes for the EB coated Mg alloy and the PVB coated Mg alloy indicates that the different passivation rate is caused by the interaction between EB and Mg alloy. From Fig. 9 we can see that the corrosion potential at the end of the measurement for the EB-coated surface is higher than that for the PVB-coated one. There are also some published results in other papers which support the notion that EB can polarize a coated Mg surface by a few hundred mV. Williams et al. found that an EB-PVB composite coating produced a potential of -0.9 V vs SHE on a pure Mg surface, while for pure Mg coated with PVB coating, the measured potential is around -1.1V vs SHE. This indicates that EB/LB couple is responsible for the oxidation of the underlying Mg. Here the schematic diagram showing the growth of EB-induced layer is presented in Fig. 11b and the major reactions are considered as following:

\[
3\text{Mg} + 4\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 \cdot 2\text{MgO} + 6e^- + 6\text{H}^+ \quad [6]
\]

\[
\text{EB}^{+} + 2\text{H}^+ + 2e^- \rightarrow \text{LB}^0 \quad [7]
\]

\[
2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2 \quad [8]
\]

EB is usually regarded as a catalytic oxidant to metal substrates. When water reaches the coating/metal interface, the interaction of Mg(OH)2 with water produces Mg2+ and OH− ions, which increases the concentration of Mg2+ ions (Eqs. 3 and 4).

**Table I.** The values of \( \delta E/\delta \log t \) for EB coated Mg alloy (EB/Mg) and PVB coated Mg alloy (PVB/Mg) upon immersion in 0.5 M NaCl solution at OCP.

| Sample (number) | EB/Mg 1 | EB/Mg 2 | EB/Mg 3 | PVB/Mg 1 | PVB/Mg 2 | PVB/Mg 3 |
|----------------|--------|--------|--------|---------|---------|--------|
| \( \delta E/\delta \log t \) | 0.3    | 0.28   | 0.27   | 0.1     | 0.13    | 0.2    |

Based on the excellent works by Taheri et al., a simple physical model showing the growth of the product layer on Mg alloy surface naturally formed after exposure in 0.5 M NaCl solution is shown in Fig. 11a. It is assumed that when bare Mg is exposed to the corrosive electrolyte, the anodic oxidation of Mg to both MgO and Mg2+ takes place first. Aging in water may cause incomplete hydration of MgO to Mg(OH)2. In addition, the precipitation of Mg2+ ions, which have transported through the permeable MgO film and entered the electrolyte, also results in the formation of Mg(OH)2 layer.

\[
\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \quad [3]
\]

\[
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad [4]
\]

\[
\text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2 \quad [5]
\]
Figure 10. OCP-t curves of EB/Mg alloy in various concentration of NaCl solution at 25°C (a-d), the insert is variation of OCP with logarithm of time, and (e) is the dependence of $\partial E/\partial \log t$ on NaCl concentration.

Figure 11. Schematic diagrams showing the growth behavior of the naturally generated oxide layer (a) and the EB-induced protective layer (b).
EB and Mg alloy occurs synchronously, where EB withdraws electrons working in a cathodic reaction and Mg produces them by anodic dissolution. For one unit of EB, i.e. four aniline residues, two protons and two electrons are taken up when it is reduced, as shown in reaction 7.48 Under the synergic influence of EB and water, the dissolution. For one unit of EB, i.e. four aniline residues, two protons and two electrons are taken up when it is reduced, as shown in reaction 7.48. Under the synergic influence of EB and water, the dissolution of magnesium undergoes via reaction 6 to form MgO directly and perhaps some Mg(OH)2 as well. This process is probably a solid reaction instead of the dissolution–precipitation of metal, leading to the alteration of various properties of the growing product layer, such as crystallinity, grain size, roughness or density. Eventually, a compact and stable MgO-rich layer mixed with only a small amount of Mg(OH)2 quickly grows on the alloy surface. This product layer should be more impermeable and stable than the naturally generated one; it hence effectively retards the penetration of ions or/and the hydration of MgO, leading to less formation of porous Mg(OH)2 outer layer. In addition, based on the works of Williams et al.50 and Shao et al.,2 the LB would be re-oxidized by atmospheric oxygen to its original form. This growth mechanism is proposed to be correlated to the increased complex impedance with time (Fig. 8) and the faster passivation rate (Fig. 9) for the EB-induced protective layer upon immersion. It can also explain the finding in the previous study that the MgO content and the compactness on film surface both increased with increasing EB loading in epoxy coating,8 which might be due to the improved interaction between EB and Mg causing the better growth of the protective layer.

Role of growth behavior on the corrosion resistance of EB-induced layer — From Fig. 10a–10d the stable corrosion potential acquired at the end of measurement was found to decrease with the increase of ion concentration, indicating that the protective capacity of interface layer declined commensurately. The similar decrease trend of the passivation rate and the corrosion resistance of the EB-induced layer illustrated the growth behavior of the protective film to be the better corrosion protection. It seems that even though PANI coating exists for the EB-induced protective layer upon immersion. It can also well for the EB-induced protective layer upon immersion. It can also well

Conclusions

The growth behavior of initial product layer formed at EB/Mg alloy interface was investigated. It was suggested that the interaction between EB and Mg could promote the rapid formation of a stable MgO-rich layer mixed with some Mg(OH)2 mainly by solid reaction instead of dissolution–precipitation. This growth mechanism was consistent with the observed results that the EB-induced protective layer exhibited a faster passivation than the naturally generated one, and less Mg(OH)2 was found in the outer layer while MgO was predominant in the bulk film.

Acknowledgments

The financial support from the National Natural Science Foundation of China (grant No. 51321062) is greatly appreciated. Yizhong Luo also acknowledges financial support by the CAS-MPG Doctoral Promotion Programme Fellowship and Dr. Adnan Sarfraz for performing the XPS measurements.

References

1. S. Sathyarayanan, S. S. Azim, and G. Venkatachari, Appl. Surf. Sci. 253, 2113 (2006).
2. Y. Shao, H. Huang, T. Zhang, G. Meng, and F. Wang, Corros. Sci. 51, 2906 (2009).
3. X. Chen, K. Shen, and J. Zhang, Pigm. Resin. Technol. 39, 322 (2010).
4. Y. Zhang, Y. Shao, T. Zhang, G. Meng, and F. Wang, Corros. Sci. 53, 3747 (2011).
5. Y. Zhang, Y. Shao, T. Zhang, G. Meng, and F. Wang, Prog. Coat. Tech. 76, 804 (2013).
6. Y. Zuo, Y. Sun, J. Li, X. Yang, J. Li, and F. Wang, Appl. Surf. Sci. 328, 247 (2015).
7. S. Sathyarayanan, S. Syed Azim, and G. Venkatachari, J. Coat. Technol. Res. 5, 471 (2008).
8. H. Wang, R. Akid, and M. Gobara, Corros. Sci. 52, 2565 (2010).
9. B. Wesling, Advanced Materials 6, 226 (1994).
10. F. Malti, S. Jasty, and A. J. Epstein, Synthetic Met 85, 1323 (1997).
11. G. Williams, R. J. Holness, D. A. Worsley, and H. N. McMurray, Electrochim. Comm. 6, 549 (2004).
12. T. C. Huang, T. C. Yeh, H. Y. Huang, W. F. Li, Y. C. Chou, W. I. Hung, J. M. Yeh, and M. H. Tsai, Electrochim. Acta 56, 10151 (2011).
13. T. C. Huang, T. C. Yeh, H. Y. Huang, W. F. Li, T. C. Lin, C. A. Chen, T. I. Yang, and J. M. Yeh, Electrochim. Acta 63, 185 (2012).
14. W. Peng, K. C. Chang, C. F. Weng, M. C. Lai, C. H. Hsu, S. C. Hsu, Y. H. Hsu, W. I. Hung, Y. Wei, and J. M. Yeh, Electrochim. Acta 95, 192 (2013).
15. C. Pan, L. Yi, S. G. Wang, and F. H. Wang, Electrochim. Acta 56, 7740 (2011).
16. A. Palacios-Padrós, F. Caballero-Briones, I. Diez-Perez, and F. Sanz, Electrochim. Acta 111, 837 (2013).
17. K. Fushimi, K. Kurashii, Y. Yamamoto, T. Nakashii, Y. Hasegawa, and T. Ohtsuka, Electrochim. Acta 144, 56 (2014).
18. S. D. Zhang, Z. W. Liu, Z. M. Wang, and J. Q. Wang, Corros. Sci. 83, 111 (2014).
19. G. T. Burstein and R. J. Cinderey, Corros. Sci. 32, 1195 (1991).
20. G. T. Burstein and R. J. Cinderey, Corros. Sci. 33, 475 (1992).
21. R. J. Cinderey and G. T. Burstein, Corros. Sci. 33, 493 (1992).
22. R. J. Cinderey and G. T. Burstein, Corros. Sci. 33, 499 (1992).
23. G. T. Burstein and C. Liu, Corros. Sci. 37, 1151 (1995).
24. G. T. Burstein and R. M. Organ, Corros. Sci. 47, 2932 (2005).
25. E. E. Abd El Aal, Corros. Sci. 50, 41 (2008).
26. S. M. Abd El Haleem, E. E. Abd El Aal, S. Abd El Wanees, and A. Diab, Corros. Sci. 52, 3875 (2010).
27. S. M. Abd El Haleem, S. Abd El Wanees, E. E. Abd El Aal, and A. Diab, Corros. Sci. 52, 292 (2010).
28. S. M. Abd El Haleem, S. Abd El Wanees, E. E. Abd El Aal, and F. Farouk, Corros. Sci. 68, 1 (2013).
29. E. E. Abd El Aal, S. Abd El Wanees, A. Farouk, and S. M. Abd El Haleem, Corros. Sci. 68, 14 (2013).
30. S. M. Abd El Haleem, S. Abd El Wanees, and A. Bahgat, Corros. Sci. 75, 1 (2013).
31. S. M. Abd El Haleem, S. Abd El Wanees, and A. Bahgat, Corros. Sci. 87, 321 (2014).
32. Y. Zuo, R. Pang, W. Li, J. P. Xiong, and Y. M. Tang, Corros. Sci. 50, 3322 (2008).
33. N. Cabrera and N. F. Mott, Rep. Prog. Phys. 12, 163 (1948).
34. J. M. A. E. Kader and A. M. S. E. Din, British Corrosion Journal 14, 40 (1979).
35. M. Taheri, R. J. Kish, N. Birbilis, M. Danaei, E. A. McNally, and J. R. Merdierid, Electrochim. Acta 116, 396 (2014).
36. M. Taheri, R. C. Phillips, R. J. Kish, and G. A. Bottom, Corros. Sci. 59, 222 (2014).
37. G. Williams and H. N. McMurray, Electrochim. Solid-State Lett. 8, B425 (2006).
38. G. Williams and R. Grace, Electrochim. Acta 56, 1894 (2011).
39. E. Y. Tallman, G. Spinks, A. Domnis, and G. W. Wallace, J. Solid State Electrochim. 6, 73 (2002).
40. G. Williams, H. N. McMurray, and A. Bennett, Mater. Corros. 65, 401 (2014).
41. R. J. Holness, G. Williams, D. A. Worsley, and H. N. McMurray, J. Electrochem. Soc. 162, 873 (2005).
42. G. Williams, A. Gabriel, A. Cook, and H. N. McMurray, J. Electrochem. Soc. 153, B245 (2006).