Self-Healing Coatings Prepared by Loading Interphase Inhibitors into MAO Coating of AM60 Mg Alloy

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A type of self–healing coating for AM60 Mg alloy was prepared by loading interphase inhibitors into micro–arc oxidation (MAO) coating. The effects of inhibitor species, impregnation methods, and MAO status on the self–healing properties of the coatings were studied using electrochemical impedance spectroscopy, scanning electron microscopy, and X–ray photoelectron spectroscopy. The results showed that, among the three selected inhibitors, Na3PO4 is the most efficient inhibitor as it forms a long–lasting protective product film Mg3(PO4)2 in the scratched areas. In comparison with atmospheric impregnation, vacuum impregnation can efficiently load inhibitors into MAO pores both in quantity and depth. Although the large size of MAO pores is harmful to the corrosion resistance of MAO coating, it is beneficial for the self–healing properties owing to the easy loading of inhibitors.

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Manuscript submitted February 15, 2018; revised manuscript received May 11, 2018. Published May 23, 2018.

Mg alloys have a promising prospect in transportation, electronics, and aerospace industries owing to their low density and high comprehensive properties.1,2 However, their further applications are significantly limited owing to their poor corrosion resistance. Many coatings have already been developed to improve the corrosion resistance of Mg alloys and most of them efficiently delay the corrosion damage by providing protective barriers against corrosive media.3,7,12 For example, there is no apparent corrosion observed on the surface of Mg alloys protected with either micro–arc oxidation (MAO) coatings even after immersion in 3.5 wt% NaCl for 2 weeks8 or organic coating after immersion for over 1 month.9 However, the lifetime of such Mg alloy parts is yet to be investigated. One of the most important reasons is that coatings are unavoidably broken in the process of transportation, installation, and application.8,10 Once coatings are broken, Mg alloys tend to undergo localized corrosion at the exposed Mg substrate,11–13 which would result in the peeling of upper paint and acceleration of the failure of Mg parts. Smart protection coatings, also referred to as self–healing coatings, can stop the initiation and propagation of corrosion generated from the broken areas.14

Self–healing coatings usually contain inhibitors as heal reagents. For example, many conversion films such as chromate,15 phosphate–permanganate,16 vanadium,17 and stannate18 conversion films show self–healing property owing to the residual15,16 and dissolution18 of interphase inhibitors. However, the self–healing property obtained from single conversion films is still limited. In comparison with conversion films, MAO coating is much more resistant to corrosion,8,19,20 MAO coating is also a type of potential self–healing coating because its outer porous layer21 is an ideal container for inhibitors. Some inhibitor–containing MAO coatings have been developed by researchers. Lamaka et al. improved the protection property of sol–gel coated MAO coating by incorporating Ce(NO3)3 into MAO coating.22 However, this improved coating can only provide protection last for 2 weeks even in 0.05 M NaCl solution. Gnedenkov et al. improved the corrosion resistance and self–healing property by incorporating 8–hydroxyquinoline into MAO.23,24 However, the surface of this porous MAO coating was not sealed, which is different from most application conditions. Ivanou et al. loaded 1,2,4–triazole into MAO coating and sealed this porous coating via sol–gel coating,25 thus obtaining improved properties, but the long–term protective ability against artificial defects has not been investigated and the loaded interphase inhibitors are easily exhausted by the flow of corrosive mediums. Therefore, these studies prove that self–healing coatings prepared by loading inhibitors into MAO pores are feasible, but the protection ability need to be further improved and many related issues should be investigated in detail.

First, the loaded inhibitors should be efficient and long–lasting. A suitable inhibitor is the key for achieving good self–healing property. In contrast to interface inhibitors, many interphase inhibitors such as phosphate,26,27 vanadate28,29 and Ce (III)30,31 are film–forming reagents for conversion films, and they can form surface films to provide long–lasting protection.26 If these interphase inhibitors are loaded into the pores of MAO coatings, they can be released to passivate the exposed Mg substrate when the Mg alloy parts are scratched. Consequently, the self–healing property may be enhanced.

Second, the inhibition efficiency usually increases with the increase in inhibitor concentrations at low concentration levels.20 Thus, it is necessary to determine an efficient method to load more inhibitors into the small pores of MAO coating. Generally, an inhibitor solution can be impregnated into pores by using atmospheric impregnation based on the principle of capillary effect.12–24 However, the pores of MAO coating are semi–closed.12 The air within the pores will hinder the loading of an inhibitor solution during impregnation. In other words, by using atmospheric impregnation, the inhibitor solution cannot reach the space occupied by air. If the pores are vacuumized in advance, an inhibitor solution can be impregnated into the pores more successfully, resulting in the increase in impregnation efficiency and the improvement of self–healing property.

Third, the pore sizes and thickness of MAO coating may have a significant influence on the self–healing property of the damaged coatings. On the one hand, these pores act as passages for corrosive media entering the coatings.3 Thus, larger pores can transport more corrosive media, leading to more severe corrosion. On the other hand, larger and deeper pores can hold more inhibitors, leading to the enhancement of self–healing property. Therefore, the influence of pore status on the self–healing property should be clarified.

In this study, three promising interphase inhibitors for Mg alloys–phosphate, vanadate, and cerium salts–were loaded into the pores of MAO, and thereafter, their self–healing abilities were compared to determine the most efficient inhibitor. Moreover, the influences of impregnation methods and pore status of MAO on the self–healing ability were investigated. To simulate the possible service conditions, the surface of MAO was sealed with an eco–friendly water–based paint. These results can provide a valuable reference for industrial applications and scientific research.

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Experimental

Samples.—Commercial cast AM60 (Al: 5.84 wt%, Mn: 0.25 wt%, Zn 0.12 wt%, Fe < 0.004 wt%, Cu < 0.008 wt%, Ni < 0.001 wt%, Be < 0.0005 wt% and Mg balance) was cut to the dimensions 30mm × 30mm × 10mm. All the exposed surfaces were mechanically ground to 2000 # with SiC paper, washed with distilled water, degreased with ethanol, and dried in a cold air flow.

The MAO coatings were prepared below 40°C with a WHD–20 MAO AC pulse power supply using the working sample as the anode and a stainless–steel plate as the cathode. The electrolyte consisted of 5 g/L NaH2P2O7, 5 g/L NaF, and 30 g/L C6H12N4. In order to obtain different pore status, four electrical parameter processes were used in this study. A constant current density of 2 A/dm2 up to a certain finial voltage and subsequent constant voltage for 100 s were applied during the MAO processes. After the MAO treatment, the samples were washed with distilled water at room temperature and dried in cold air. The number, electrical parameters, and status of the four kinds of samples are listed in Table I. Mostly, the MAO treatment process # 2 was used for the investigation, except for the comparison of pore status.

The porous MAO coatings were impregnated with 0.5 M inhibitors Ce(NO3)3, Na3PO4, and NaVO3 with pH values of 1.72, 12.54, and 6.35, respectively. Two types of impregnation methods, vacuum impregnation and atmospheric impregnation, were applied. For atmospheric impregnation, the samples were immersed in inhibitor aqueous solution for 10 min. For vacuum impregnation, the samples were placed in a filter flask, which was constructed as shown in Fig. 1, and subsequently, the device was vacuumized when the valve was closed. After the barometric pressure was maintained below 10 kPa for 1 h, the valve was opened to suck the inhibitor solution into the filter flask and submerge the samples. The samples were immersed for 10 min and thereafter exposed to atmosphere. After impregnation, to avoid a negative effect on the adhesion with the upper paint, all the impregnated samples were washed twice with distilled water to remove the residual salts on the surface, washed with ethanol to accelerate the speed of drying, and thereafter dried in hot air. Finally, a commercial water–based paint mixed with epoxy resin and polyamide resin was applied on the impregnated MAO coatings using brushing. The thickness of the dry paint films was approximately 80 ± 5 μm. Mostly, vacuum impregnation was used for the investigation, except for the comparison of the impregnation methods.

The obtained MAO–based coatings are denoted as composite coatings in this paper and several types of composite coatings were prepared according to the methods described above: (1) blank MAO sealed with paint, denoted as MAO_paint; (2) inhibitor–containing MAO sealed with paint, denoted as Ce@MAO_paint, P@MAO_paint, and V@MAO_paint for loading Ce(NO3)3, Na3PO4, and NaVO3 into the pores of MAO via vacuum impregnation, respectively; (3) P@MAO_paint was used for the comparison of different impregnation processes and pore status; (4) in order to investigate the self–healing mechanism, NaOH–containing composite coating, denoted as NaOH@MAO_paint, was prepared by impregnating NaOH into MAO via vacuum impregnation.

Evaluation of composite coatings.—Preparation of artificial defects.—In order to investigate the self–healing process, artificial defects on the surface of the composite coatings were prepared using a lathe tool before the corrosion experiments. The scratches were approximately 200 μm in width and 1.8 cm in length with a top angle of 90°. Mg substrate was exposed at the bottom of the scratches. To probe the self–healing products by X–ray photoelectron spectroscopy (XPS), the artificial defects of composite coating were prepared by drilling a hole to AM60 substrate with diameter of 1 mm.

Characterization of coatings and corrosion products.—The thickness of the composite coatings was determined using a digital thickness gauge TT210. The thickness and pore size of the MAO coatings were determined by the observation of cross–sectional morphologies using a scanning electron microscope (SEM; Philips XL30FEG).

The coating adhesion was measured using Zwick/Roell Z505 Universal Testing Machine with working area of 3.14 cm2. In order to characterize the loading efficiency of inhibitors, the cross–sectional back scattered electron (BSE) morphology of Ce(NO3)3–loaded MAO coatings were observed using SEM.

The corrosion products around the scratched sites were observed using SEM equipped with energy–dispersive X–ray spectroscopy (EDX) with an acceleration voltage of 14 kV. In addition, the self–sealing products around the damaged areas were probed using ESCALAB 250 XPS with the use of Al Kα radiation. The power was 150W. The energy values were corrected according to the adventitious C 1s signal, which was set at 284.60 eV.

Evaluating the self–healing.—In order to evaluate the self–healing effect, the artificial scratches were prepared by a lathe tool before the corrosion experiments. The scratches were approximately 200 μm in width and 1.8 cm in length with a top angle of 90°. Mg substrate was exposed at the bottom of the scratches. The self–healing process was examined using a scanning electron microscope (SEM; Philips XL30FEG). The coating adhesion was measured using Zwick/Roell Z505 Universal Testing Machine with working area of 3.14 cm2. In order to characterize the adhesion force of inhibitors, the self–healing products around the damaged areas were probed using ESCALAB 250 XPS with the use of Al Kα radiation. The power was 150W. The energy values were corrected according to the adventitious C 1s signal, which was set at 284.60 eV.

Electrochemical measurements.—Electrochemical impedance spectroscopy (EIS) measurements were carried out to investigate the corrosion process of the MAO coatings and scratched composite coatings using a PARSTAT4000 electrochemistry test system (Princeton Applied Research, USA). The samples were sealed with silicone rubber with an exposed surface area of 2.54 cm2 (for the composite coatings, the length of the scratches was the diameter) and thereafter immersed in 3.5 wt% NaCl solution, which was not updated during immersion. A typical three–electrode electrochemical cell was used with the sample as the working electrode, a platinum plate as the counter electrode, and a saturated calomel electrode as the reference electrode. EIS measurements were carried out at OCP using a single sinusoidal excitation signal of amplitude 15 mV with the frequency

Table I. Electrical parameters and status of MAO coatings.

| No. | Frequency (Hz) | Duty cycle (%) | Final voltage (V) | Time of first step (min) | Constant voltage (V) | Thickness (μm) | Proportion of pores area (surface) (%) | Pore diameter (surface) (μm) | Pore depth (μm) |
|-----|---------------|----------------|------------------|-------------------------|---------------------|--------------|-------------------------------------|--------------------------|--------------|
| # 1 | 600           | 20             | 400              | 8                       | –                   | 9.1          | 3.19                                | 0.89                     | 2.0          |
| # 2 | 500           | 30             | 400              | 8                       | 400                 | 9.5          | 4.39                                | 0.97                     | 5.3          |
| # 3 | 900           | 30             | 400              | 7                       | 400                 | 11.8         | 4.61                                | 0.98                     | 6.3          |
| # 4 | 600           | 20             | 440              | 11                      | 440                 | 16.2         | 6.57                                | 1.20                     | 8.7          |

Figure 1. Sketch map of vacuum impregnation device.
Figure 2. EIS spectra of the scratched composite coatings after immersion in 3.5 wt% NaCl for 24 h, these coatings contained different inhibitors of Ce(NO$_3$)$_3$, Na$_3$PO$_4$ and NaVO$_3$.

varied from 100 kHz to 10 mHz for the scratched composite coatings and from 100 kHz to 100 mHz for the MAO coatings. The different frequency ranges were set because the regular plots below 100 mHz were difficult to obtain for MAO coatings. All the impedance data were fitted using ZsimpWin software according to appropriate equivalent circuits. Although the electrochemical results were mainly associated with the exposed Mg, the entire working area of 2.54 cm$^2$ rather than the scratched area of 0.036 cm$^2$ was used to analyze the EIS results of the scratched composite coatings. All the results were obtained by performing more than three experiments.

Results and Discussion

**Effects of inhibitor species on the self–healing ability.**—The loading capacity of inhibitors in the pores of MAO coatings is small. Thus, it is necessary to select an efficient inhibitor to achieve high self–healing ability. The reagents for preparation of conversion films are available for this aim because they can passivate the Mg substrate well. Therefore, three inhibitors, Ce(NO$_3$)$_3$, Na$_3$PO$_4$, and NaVO$_3$, were selected as heat reagents to fill the pores. In order to evaluate the self–healing ability, Nyquist plots of the scratched MAO$_{paint}$, Ce@MAO$_{paint}$, P@MAO$_{paint}$, and V@MAO$_{paint}$ after immersion in 3.5 wt% NaCl solution for 24 h are shown in Fig. 2. For P@MAO$_{paint}$, the plot consisted of two capacitance loops. For MAO$_{paint}$, Ce@MAO$_{paint}$, and V@MAO$_{paint}$, all the plots consisted of two possible capacitance loops and an inductance loop, and their dimensions were much smaller than that of P@MAO$_{paint}$. As the EIS results mainly exhibited the corrosion behavior of the exposed Mg at the scratched areas, the high–frequency capacitance loop is related to the electric double layer at the interface of the exposed Mg substrate and corrosive medium, the medium–frequency capacitance loop is related to the product film, and the low–frequency inductance loops indicate the initiation of corrosion. From the comparison of the EIS spectra, especially the inductance loops, the scratched areas of P@MAO$_{paint}$ were observed to remain in good condition whereas the scratched areas of MAO$_{paint}$, Ce@MAO$_{paint}$, and V@MAO$_{paint}$ were observed to be corroded.

The SEM image of the scratched areas of the MAO$_{paint}$ sample before immersion is shown in Fig. 3a and those of the scratched areas of the four composite coatings after immersion in 3.5 wt% NaCl for 24 h are shown in Figs. 3b–3g. After scratching, the exposed substrate and exposed MAO could be observed on the scratched areas of the MAO$_{paint}$ sample (Fig. 3a). This is similar to Figs. 3d–3e, indicating that the loading of inhibitors did not worsen the adhesion of upper paint. After immersion for 24 h, the scratched areas of the MAO$_{paint}$ sample were corroded severely (Fig. 3b). When inhibitors were loaded (Figs. 3c–3e), abundant cracks were visible in the product films near the exposed MAO coatings, indicating that the product films were thick at these places. However, there was a significant difference in the smooth regions of the scratches of the three samples. For the Ce@MAO$_{paint}$ sample shown in Fig. 3c, many small grooves, especially obvious localized corrosion, could be observed, but the corrosion was much gentler than that of the MAO$_{paint}$ sample (Fig. 3b). This indicated that a film was formed in the scratched areas. However, the film was too thin to cover the exposed Mg substrate completely in view of the presence of small grooves. Consequently, localized corrosion could be initiated from the weak sites of the film. For the P@MAO$_{paint}$ sample, the scratched areas were uniform and smooth with small grooves, and there was no obvious corrosion (Fig. 3d). The product film with cracks could be observed in the smooth areas from the high–magnification morphology in Fig. 3f. The Nyquist plots of the scratched P@MAO$_{paint}$ sample after immersion in 3.5 wt% NaCl for different durations are shown in Fig. 4a. For immersion until 7 d, the Nyquist plots consisted of two capacitance loops without an inductance loop. After immersion for 11 d, a low–frequency inductance loop appeared, indicating the initiation of corrosion. As the product film was uneven with some cracks, a circuit with (R$_Q$Q$_f$) in parallel (the equivalent circuit (1) in Fig. 4a) was used to fit the EIS plots for 1 d, 4 d, and 7 d. A circuit with (R$_Q$Q$_f$) in parallel with (R$_L$L) (equivalent circuit (2) in Fig. 4a) was used to fit the EIS plots for 11 d. In these equivalent circuits, R$_Q$, R$_f$, and R$_L$ refer to the resistances of the solution, charge transfer, and surface film, respectively; Q$_f$ refer to the capacitances of the electric double layer and product film, respectively; L and R$_L$ refer to the inductance of the electrochemical reactions at the film/substrate interface and the resistance of the inductance, respectively. Constant phase elements Q are used to replace capacitors to compensate for the inhomogeneity. Q is defined by two values, Y and n. If n is equal to 1, Q is identical to a capacitor (C). The variations of the fitted R$_Q$ and R$_f$ values are shown in Fig. 4b. It could be observed that the R$_Q$ values, which are associated with the charge transfer process, first decreased with the increase in immersion time from 1 d to 4 d, thereafter remained stable until 7 d, and finally decreased sharply once corrosion occurred after 11 d. The R$_f$ values, which are associated with the surface film formed at the scratched areas, first decreased, thereafter increased to reach the maximum at 7 d, and finally decreased sharply after 11 d. The variation trends of the R$_Q$ and R$_f$ values during immersion for 4 d to 7 d demonstrated the self–healing processes around the scratched areas; the protective film was formed gradually, and thereafter degraded after long–term immersion. The exposed Mg substrate could remain intact after immersion in 3.5 wt% NaCl solution for more than one week. In the actual applications, if the service condition is much gentler than 3.5 wt% NaCl, the scratched Mg parts will retain in a good condition for a long time. This indicated that the scratched P@MAO$_{paint}$ sample might exhibit good self–healing property under real service environments.
Figure 3. SEM micrographs of the scratched areas of MAO_paint (a) and scratched areas after immersion in 3.5 wt% NaCl for 24 h: (b) MAO_paint; (c) Ce@MAO_paint; (d) P@MAO_paint; (e) V@MAO_paint. (f) magnified SEM morphologies of area A in P@MAO_paint; (g) magnified SEM morphologies of area B in V@MAO_paint.

The better self-healing property of P@MAO_paint can be attributed to two possibilities. One is that the high alkalinity of 0.5 M Na₃PO₄ solutions with pH 12.54 may passivate the damaged areas by the formation of Mg(OH)₂ film, leading to the improvement of self-healing property. Another is the formation of relatively compact film of phosphate product.

To prove the first possibility, a comparative study was presented by impregnating NaOH at pH 12.54 into MAO, which was denoted as NaOH@MAO_paint. The EIS plot of the scratched NaOH@MAO_paint after immersion in 3.5 wt% NaCl for 24 h is shown in Fig. 5. It could be seen that an inductance loop was detected, indicating the naturally formed film in the scratched areas were broken after immersion for 24 h. Also, the dimension of the Nyquist plot of NaOH@MAO_paint was much smaller than that of P@MAO_paint. This meant that the formation of Mg(OH)₂ in NaOH solution could not provide enough self-healing property.
To prove the second possibility, MAO_paint and P@MAO_paint with holes of 1 mm reaching the AM60 substrate were immersed in 3.5 wt% NaCl for 24 h and then the hole areas were examined by XPS. As holes were prepared by drilling, MAO coating was not exposed to the XPS probe. The high–resolution spectra of P 2p and O 1 s are shown in Fig. 6. It could be seen that there was no obvious P 2p peak in MAO_paint sample, which meant that the high chemical stability of phosphate constituents in the MAO coating could not be released to heal the damaged areas. However, the P@MAO_paint sample showed a peak at approximately 133.8 eV which could be attributed to Mg3(PO4)2 in the film. In addition, the O 1 s peak of self–healing P@MAO_paint could be divided into three peaks, 535.7 eV for Mg(OH)2,40,41 and 533.4 eV for phosphate.42 This indicated that Na3PO4 inhibited the corrosion of the scratched areas by formation of Mg3(PO4)2.38 In addition, the O 1 s peak of self–healing P@MAO_paint showed a peak at approximately 133.8 eV which could be attributed to upper paint, 532.0 eV for Mg(OH)2,40,41 and 533.4 eV for phosphate.42 This indicated that Na3PO4 inhibited the corrosion of the scratched areas by formation of Mg3(PO4)2.

In order to describe the possible self–healing mechanism, the schematic illustrations of P@MAO_paint and its self–healing process are shown in Fig. 7. The evolution of scratched areas includes three processes: (I) the formation and breakdown of Mg(OH)2; (II) the reduction of Mg2+ to Mg(OH)2; (III) the reduction of phosphate concentration and the inhibition efficiency. The detailed processes are discussed below.

AM60 mainly consists of the primary α–Mg matrix and Mg17Al12/AlxMny intermetallic particles.30 As the impurity level (Fe, Ni, Cu) is extremely low, and Mn can also depress the effect of Fe by forming intermetallic compound, the negative effects of impurities can be ignored.43 As a result, anodic dissolution mainly occurs on the α–Mg matrix phase according to Reaction 1. Cathodic hydrogen evolution is more likely to take place on the intermetallic particles according to Reaction 2. Once the exposed AM60 around the scratched areas is immersed in the 3.5 wt% NaCl, a relatively loose and thick layer of Mg(OH)2 film is formed on the surface of the α–Mg matrix according to Reaction 3.

\[ Mg = Mg^{2+} + 2e^- \]  
\[ 2H_2O + 2e^- = H_2 + 2OH^- \]  
\[ Mg^{2+} + 2OH^- = Mg(OH)_2 \]

The continuity of this film is disrupted by the presence of the intermetallic particles on the surface44 (the cracks in Figs. 7a, 7b). Besides, Mg(OH)2 film will be broken naturally by the attack of Cl−.45 Then, Mg is dissolved from the cracks and broken areas preferentially. The above description can be shown in Fig. 7a.

With the immersion time is increased, the corrosive solution permeates into MAO pores from the cross–section of the scratches, and subsequently, phosphate is dissolved and released into the scratched areas. Thereafter, the released phosphate combines with the dissolved Mg2+ in the cracks and broken areas preferentially to form relatively compact and dense Mg3(PO4)2 according to Reaction 4.26,27 This process is described in Figs. 7b, 7c.

\[ 3Mg^{2+} + 2PO_4^{3-} = Mg_3(PO_4)_2 \]

In the early stage of inhibitor release, the phosphate was insufficient. The formation rate of Mg3(PO4)2 was slower than the breakdown rate of Mg(OH)2, resulting in the decrease in Rf and Rd during immersion for 1 d to 4 d (Fig. 4b). When the immersion time was longer, the inhibitors loaded near the scratched areas were released completely as shown in Fig. 7d. Phosphate could no longer be released and the concentration of phosphate decreased because of its consumption. Thus, the inhibition efficiency decreased. In addition, the attack ability of Cl− to film is still strong. Consequently, the film would fail after long–term immersion, corresponding to the sharp decrease in Rf and Rd after immersion for 11 d (Fig. 4b).

![Figure 4. EIS spectra (a) and variations of charge transfer resistance $R_t$ and coating resistance $R_f$ of the scratched P@MAO_paint after immersion in 3.5 wt% NaCl for different time. The inserted equivalent circuit (1) in Fig. 4a is related to immersion time of 1, 4, and 7 d, and equivalent circuit (2) is related to immersion time of 11 d.](image)

![Figure 5. EIS spectrum of the scratched NaOH@MAO_paint after immersion in 3.5 wt% NaCl for 24 h.](image)
Effects of impregnation processes on the self–healing ability.— The pore sizes of MAO are at the micrometer scale. Thus, the spaces for loading inhibitors are very small. In the published works, atmospheric impregnation was used to fill the inhibitors into the pores, and the loading capacity was low. In order to increase the load efficiency, vacuum impregnation was employed and was compared with atmospheric impregnation in this section. The EIS plots of the scratched composite coatings prepared using both methods were measured after immersion in 3.5 wt% NaCl for different terms. The Nyquist plots for immersion of 24 h are shown in Fig. 8a. Both plots consisted of two capacitance loops and no inductance loops, indicating that the exposed Mg was not corroded during immersion for 24 h. As the inhibition efficiency increases with the increase in phosphate concentration at low concentration levels, the variation of inhibition efficiency is equal to the load efficiency. Hence, the larger dimension of Nyquist plot of the vacuum impregnation samples indicated that vacuum impregnation had an advantage over atmospheric impregnation. The variations of the low–frequency impedance modulus $|Z|$ (at 0.01 Hz) during immersion are presented in Fig. 8b. $|Z|$, the $|Z|$ values of the vacuum impregnation samples, first decreased during immersion for 1 d to 4 d, thereafter increased during immersion for 4 d to 7 d, and finally decreased sharply after immersion for 11 d. This trend indicated good self–healing ability as explained before. However, $|Z|$, the $|Z|$ values of the atmospheric impregnation samples, always decreased with the increase in immersion time. Especially, a sharp decrease was observed for immersion of 7 d. In other words, $|Z|$, always larger than $|Z|$, and decreased at a slower rate as well, indicating that vacuum impregnation was superior to atmospheric impregnation both during short–term and long–term immersion.

Figure 6. XPS high–resolution spectra of the formed film in damaged areas: (a) P 2p of MAO_paint and P@MAO_paint; (b) O 1s of P@MAO_paint.

Figure 7. Schematic illustrations of P@MAO_paint sample and the self–healing process: (a) the formation and damage of cracked Mg(OH)$_2$ film; (b) the inhibition mechanism of Na$_3$PO$_4$ in published paper; (c) the release of inhibitor and the formation of Mg$_3$(PO$_4$)$_2$; (d) the final structure of scratched areas and the exhaustion of inhibitor.
The impregnation process had been carried out once in the above investigation. It can be speculated that the impregnation efficiency may be affected by the impregnation frequency. Therefore, different vacuum impregnation frequencies i.e., once, twice, and thrice were compared in this section. In each impregnation period, samples were impregnated in vacuum and dried in atmosphere. The Nyquist plots of the scratched composite coatings with different impregnation times after immersion in 3.5 wt% NaCl for 24 h are shown in Fig. 9. All the three plots consisted of two capacitance loops and no inductance loops, indicating that the scratched areas were not corroded. However, it was evident that the dimensions of the Nyquist plots did not increase with the increase in impregnation frequency; furthermore, the excessive frequency of three times even had a negative effect. To clarify the possible reason, the impregnation process is described in detail.

It is easy to understand that MAO can be impregnated with more inhibitor solution via vacuum impregnation. When a semi-closed micro–pore is submerged in a solution, the solution can enter the micro–pore owing to the capillary effect. The schematic force illustration during the impregnation is presented in Fig. 10a. Before impregnation, the pressure inside and outside the pore is equal to the vacuum pressure P. After the immersion of the inhibitor solution, the solution depth can be derived as follows:

\[ h = H \left(1 - \frac{P}{\frac{2\alpha \cos \theta}{r} + P_0}\right) \]  

where R is calculated using the geometric relation

\[ R = r \cos \theta \]  

Usually, \( P_0 = 10^5 \text{ Pa} \), \( \rho = 10^3 \text{ kg m}^{-3} \), \( g = 10 \text{ m s}^{-2} \), \( h = 10^{-6} \text{ m} \), \( r = 10^{-6} \text{ m} \), and \( \alpha = 10^{-2} \text{ N m}^{-1} \) in this condition. Therefore, gravity can be neglected because its contribution to \( F_D \) is negligible.

Further, the upward total force \( F_U \) can be calculated using barometric pressure as follows:

\[ F_U = P' \pi r^2 \]  

where \( P' \) can be calculated using the ideal gas equation

\[ P'(H-h)\pi r^2 = PH\pi r^2 \]  

When balance is achieved, \( F_D = F_U \).

\[ P_0\pi r^2 + \frac{2\alpha \cos \theta}{r}\pi r^2 = \frac{H}{H-h}P\pi r^2 \]  

Finally, the solution depth can be derived as follows:

\[ h = H \left(1 - \frac{P}{\frac{2\alpha \cos \theta}{r} + P_0}\right) \]  

We suppose that the depth of the semi–closed pores is 5 \( \mu \text{m} \), radius is 0.5 \( \mu \text{m} \) (the parameter of # 2 MAO coating in Table 1), surface tension coefficient of solution is 72.06 mN/m (the parameter of deionized water), and contact angle is 20°. When the solution is impregnated under different negative pressures and thereafter dried in atmosphere where \( P_0 = 100 \text{ kPa} \), the calculated impregnation depths under different impregnation pressures are presented in Fig. 10b. It can be observed that, when the impregnation pressure decreases from 100 kPa to 10 kPa, the impregnation depth increases from 3.65 \( \mu \text{m} \) to 4.87 \( \mu \text{m} \). This not only indicates that more inhibitor solution is absorbed, but also indicates that the inhibitor solution can reach the bottom of the pore more closely. When the inhibitor reaches sufficiently deeply into the pores, it is difficult to eliminate during the subsequent clean step. Moreover, once the composite coatings are broken, the inhibitor closer to the bottom of the pores can be released closer to the exposed substrate, thus increasing the self-healing ability.

In order to prove the calculated impregnation results according to the equation above, the loading capacities of atmospheric and vacuum impregnation samples were compared. Because there exit some...
phosphate constituents in the MAO coating, it would disturb the real loading capacities if the P@MAO_paint sample was used for this comparison. Thus, Ce(NO\textsubscript{3})\textsubscript{3} was filled into MAO pores by atmospheric impregnation and vacuum impregnation, and then the cross-sectional morphologies were observed using SEM as shown in Fig. 11. It could be seen that the pores A and B in atmospheric impregnation sample were partially filled by the Ce constituents as the light areas. The bottom of the pores was empty, indicating that inhibitors could be filled into the upper part of the pores by atmospheric impregnation. Differently, the pores of C and D in the vacuum impregnation sample were filled by the Ce constituent completely, and the inhibitors had already reached the bottom of these pores, indicating Ce could be loaded deeper into MAO coating by vacuum impregnation. This result was consistent with the calculated impregnation results.

According to the analyses of the vacuum impregnation process, after the impregnation was carried out once, because the impregnated Na\textsubscript{3}PO\textsubscript{4} solution was almost saturated, the pores of MAO were filled with Na\textsubscript{3}PO\textsubscript{4} with no space remaining, especially at the bottom of pores, which could not be cleaned in the subsequent clean step. Moreover, when impregnation was carried out more frequently, the Na\textsubscript{3}PO\textsubscript{4} already presented in the pores will dissolve and thereafter diffuse out of the pores. Therefore, higher impregnation frequency could not increase the impregnation efficiency. Furthermore, MgO, which is the main constituent of MAO coating, could be dissolved in an aqueous solution, and excessive impregnation would deteriorate the property of MAO and even reduce the impregnation efficiency, thus weakening the property of composite coating. Thus, vacuum impregnation was superior to atmospheric impregnation and excessive impregnation had a negative effect.

Effects of pore status on the self-healing property.—In addition to the impregnation method and frequency, the status of MAO coatings significantly affects the impregnation efficiency. In theory, more inhibitors can be loaded into larger and deeper pores to enhance the self-healing property of the composite coating. Therefore, the effect of pore status on the self-healing property is discussed in this section. MAO coatings with different thicknesses and pore sizes were prepared. The SEM images of these MAO coatings are presented in Fig. 12 and the cross-sectional morphologies are presented in Fig. 13. The statistical status of MAO coatings is listed in Table I. As MAO coatings are not absolutely uniform, only the average areas are

\begin{figure}[h]
\centering
\includegraphics{figure10.png}
\caption{Schematic force illustration during vacuum impregnation (a) and the calculated impregnation depth under different impregnation pressures (b).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics{figure11.png}
\caption{BSE–SEM cross-sectional morphologies of Ce(NO\textsubscript{3})\textsubscript{3}–containing MAO coatings: Ce(NO\textsubscript{3})\textsubscript{3} was impregnated by atmospheric (a) or vacuum impregnation (b).}
\end{figure}
When the pores of these MAO coatings were loaded with Na₃PO₄ and sealed with water–based paint, the self–healing properties of these scratched composite coatings were compared using EIS measurements after immersion in 3.5 wt% NaCl for different terms. The variations of low–frequency impedance modulus (|Z|) (at 0.01 Hz) during long–term immersion are shown in Fig. 15. It was evident that the |Z| values of sample # 1 were minimum, and never increased during immersion for 7 d, which might be because the released phosphate was insufficient to heal the breakdown of Mg(OH)₂. The |Z| values of samples # 2, # 3, and # 4 were larger and increase after immersion for 4 d, which was because larger and deeper pores could hold more inhibitors. The scratched sample # 2 showed the maximum |Z| values but failed after corrosion for 11 d. Although the |Z| values of the scratched samples # 3 and # 4 were smaller than that of sample # 2, these samples were still in good condition even after immersion for 11 d. This indicated that the best corrosion resistance of the MAO coating # 2 (Fig. 14) could contribute to the protection property of the scratched areas in short–term immersion, but the long–term protection still depended on the load efficiency of inhibitors.

The optical photographs of the scratched composite coatings based on different MAO after immersion in 3.5 wt% NaCl for 15 d are presented in Fig. 16. Apparent corrosion was observed in the scratched areas of sample # 1, and the corrosion was even extended to more than 2 mm with the peeling of the upper paint. Sample # 2 showed the peeling of the upper paint near the scratched areas, indicating the initiation and gentle propagation of corrosion. In the case of sample # 3, only small corrosion sites were observed in the scratched areas. Significantly, no apparent corrosion was observed on sample # 4. Considering the optical photographs, larger and deeper pores were beneficial to the self–healing property, and sample # 4 could withstand the corrosion medium of 3.5 wt% NaCl even for over 15 d.

Usually, the pores of MAO coatings are harmful to the corrosion resistance, and hence, many studies focus on the reduction of pore sizes or sealing of pores. However, when MAO coatings are loaded with inhibitors and thereafter sealed with upper paint in actual applications, larger and deeper pores can hold more inhibitors, which may eliminate the disadvantage of pores and even increase the smart protection to the scratched areas. Therefore, the disadvantages of pores may be ignored in most actual applications.

Conclusions

The pores of MAO were used as efficient carriers of inhibitors to prepare self–healing composite coatings. Among the three interphase inhibitors Ce(NO₃)₃, Na₃PO₄, and NaVO₃, Na₃PO₄ is most efficient at prolonging the lifetime of scratched composite coatings in this condition. Compared with atmospheric impregnation, an inhibitor can be
loaded more efficiently into the pores of MAO via vacuum impregnation both in quantity and depth, leading to the increase of self–healing property. However, higher impregnation frequency is not beneficial to self–healing ability, because the bottom of pores is fully filled during the first impregnation. When the pore size of MAO coating increases, the corrosion resistance of MAO coating decreases because the pores are the passages of corrosive media entering the coating; when the pores are filled with inhibitors and sealed with upper paint, improved smart protection is provided to the scratched areas because larger pores hold more inhibitors.

Acknowledgments
This work was supported by the National Natural Science Foundation of China (No. 51671199) and the National Key Research and Development Program of China (No. 2016 YFB0301105).

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References
1. T. M. Pollock, Science, 328, 986 (2010).
2. L. Ruan, S. Ezaki, F. Masahiro, S. Shen, and Y. Kawamura, J. Magn. Alloy, 4, 27 (2016).
3. Z. J. Li, X. Y. Jing, Y. Yuan, and M. L. Zhang, Corros. Sci., 63, 358 (2012).
4. T. Ishizaki, Y. Masuda, and K. Teshima, Surf. Coat. Technol., 217, 76 (2013).
5. H. P. Duan, K. Q. Du, C. W. Yan, and F. H. Wang, Electrochim. Acta, 51, 2898 (2006).
6. C. Blawert, W. Dietzel, E. Ghali, and G. L. Song, Adv. Eng. Mater., 8, 511 (2006).
7. L. Y. Cui, S. D. Gao, P. P. Li, R. C. Zeng, F. Zhang, S. Q. Li, and E. H. Han, Corros. Sci., 118, 84 (2017).
8. K. H. Dong, Y. W. Song, D. Y. Shan, and E. H. Han, Corros. Sci., 100, 275 (2015).
9. S. V. Lamaka, M. G. S. Ferreira, and M. J. Carmezim, Surf. Coat. Technol., 200, 3021 (2006).
10. S. Hiromoto, Corros. Sci., 100, 284 (2015).
11. X. H. Guo, Q. Z. Guo, K. Q. Du, Y. Wang, and F. H. Wang, Rec Adv., 6, 39053 (2016).
12. O. V. Karavai, A. C. Bastos, M. L. Zheludkevich, M. G. Teryba, S. V. Lamaka, and M. G. S. Ferreira, Electrochim. Acta, 55, 5401 (2010).
13. S. Pommiers, J. Frayret, A. Castelbon, and M. Potin-Gautier, Corros. Sci., 84, 135 (2014).
14. E. Rocca, C. Juers, and J. Steinmetz, Corros. Sci., 52, 2172 (2010).
15. A. S. Handy, L. Doench, and H. Möhwald, Electrochim. Acta, 56, 2493 (2011).
16. N. Yang, Q. Li, F. N. Chen, P. Cai, C. Tan, and Z. X. Xi, Electrochim. Acta, 174, 1192 (2015).
17. R. F. Zhang and S. F. Zhang, Corros. Sci., 51, 2820 (2009).
18. R. F. Zhang, S. F. Zhang, and S. W. Dou, Appl. Surf. Sci., 255, 7893 (2009).
19. R. F. Zhang, Corros. Sci., 52, 1285 (2010).
20. S. V. Lamaka, G. Knönschild, D. V. Smirnova, M. G. Teryba, M. L. Zheludkevich, and M. G. S. Ferreira, Electrochim. Acta, 55, 131 (2009).
21. A. S. Gnedenkov, S. I. Sinebryukhov, D. V. Mashialyur, and S. V. Gnedenkov, Corros. Sci., 102, 269 (2016).
22. A. S. Gnedenkov, S. I. Sinebryukhov, D. V. Mashialyur, and S. V. Gnedenkov, Corros. Sci., 102, 348 (2016).
23. D. K. Ivanou, K. A. Yasakau, S. Kallip, A. D. Lisenkov, M. Shtarkovich, S. V. Lamaka, M. G. S. Ferreira, and M. L. Zheludkevich, Rsc Adv., 6, 12553 (2016).
24. G. Williams, R. Grace, and R. M. Woods, Corrosion, 71, 184 (2015).
25. A. S. Gnedenkov, S. G. Stanciu, A. A. Matei, E. K. Karaxi, R. Hristu, A. Karantonis, and C. A. Charitidi, Corros. Sci., 100, 194 (2015).
26. F. E. Heikal, A. M. Fekry, and M. Z. Fatayerji, J. Appl. Electrochem., 39, 1633 (2009).
27. D. Liu, Y. W. Song, D. Y. Shan, and E. H. Han, Int. J. Electrochem. Sci., 13, 2219 (2018).
28. F. E. Heikal, O. S. Shehata, and N. S. Tantawy, Corros. Sci., 56, 86 (2012).
29. K. Aramaki, Corros. Sci., 46, 1565 (2004).
30. J. A. Curran and T. W. Clyne, Acta Mater., 54, 1905 (2006).
31. W. Yanli, Z. Yanhao, L. Chao, S. Dalei, Z. Tao, Z. Xinran, Y. Yongde, Z. Meng, W. Jun, and D. G. Schlukin, Appl. Surf. Sci., 369, 384 (2016).
32. A. Yabuki, T. Shiraishi, and I. W. Futhona, Corros. Sci., 103, 117 (2016).
33. J. H. Liu, Y. W. Song, D. Y. Shan, and E. H. Han, J. Electrochem. Soc., 163, C856 (2016).
34. J. L. Domingo, Biol. Trace Elem. Res., 88, 97 (2002).
35. K. H. Dong, Study on the Formation Mechanism of the Self-sealing Pores Micro-arc Oxidation Film on Magnesium alloy, in, Shenyang University of Technology (2015).
36. A. Shimamura, E. Kasezaki, M. I. Jones, and J. B. Metson, J. Solid State Chem., 186, 116 (2012).
37. G. Beamson, D. T. Clark, N. W. Hayes, and D. S. Law, Surface Science Spectra, 3, 357 (1994).
38. F. E. Heikal, P. Marcus, and I. Olefjord, Surf Interface Anal., 34, 494 (2002).
39. M. F. Montemor, A. M. Simões, M. G. S. Ferreira, and M. J. Carneizim, Appl. Surf. Sci., 254, 1806 (2008).
40. W. He, E. Zhang, and K. Yang, Mater. Sci. Eng. C, 30, 167 (2010).
41. S. V. Lamaka, B. Vagehizazari, D. Mei, R. P. Petrauskas, D. Hooce, and M. L. Zheludkevich, Corros. Sci., 128, 224 (2017).
42. D. B. Huang, J. Y. Hu, G. L. Song, and X. P. Guo, Electrochim. Acta, 56, 10166 (2011).
43. L. Yang, Q. Jiang, M. Zheng, B. Hou, and Y. Li, J. Magn. Alloy., 4, 22 (2016).
44. R. F. Zhang, G. Y. Xiong, and C. Y. Hu, Curr. Appl. Phys., 10, 255 (2010).