Improved corrosion resistance of AZ91D magnesium alloy by an aluminium-alloyed coating

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Abstract

An aluminum-alloyed coating was applied onto the surface of magnesium alloy AZ91D. The coating formed in aluminium powder at 420 °C is rich in the $\beta$ ($\text{Mg}_{17}\text{Al}_{12}$) phase. Polarisation curve, AC impedance, salt immersion and salt spray were carried out to investigate the corrosion behaviour and assess the corrosion performance of the coated magnesium alloy. It was found that a coated AZ91D specimen was much more corrosion resistant and harder than an uncoated one. The improved corrosion resistance was mainly ascribed to the high volume fraction of $\beta$ phase in the coating.

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1. Introduction

Magnesium alloys have a high strength-to-weight ratio, and are promising alternatives to steel and aluminium alloys in the automotive industry. They are also being increasingly used in the electronic industry for their attractive electromagnetic and impact properties. However, poor corrosion performance is one of the critical issues limiting further application of these alloys.

To improve the corrosion resistance of magnesium alloys, a number of surface treatments have been proposed and tried [1–4], such as laser and ion beams, PVD, CVD, chemical conversion, anodisation, electro- or electro-less plating, organic coating, etc. All these surface treatments aim at modifying the surface of magnesium alloys without affecting their bulk performance. Some of these coating methods have been claimed to be able to offer good corrosion protection to magnesium alloys. Nevertheless, all these techniques have some inevitable disadvantages. For example, laser and ion beams are expensive; chemical conversion, anodisation and plating face environmental pressure; and an organic coating normally needs a chemical conversion or anodised coating to prime the substrate first. Moreover, apart from the corrosion resistance, wear resistance and electrical conductivity are also important in some applications. From a practical point of view, an ideal surface treatment is expected to meet all these demands. Unfortunately, so far such a surface treatment for magnesium alloys is still a goal not yet achieved.

Based on the understanding of the role of the $\beta$ phase ($\text{Mg}_{17}\text{Al}_{12}$) [5–8] in reducing the corrosion rate if the volume faction of the phase in the “skin” of a magnesium alloy is high enough, Song in 1997 [9] pointed out that if an alloy would become very resistant to corrosion without sacrificing its mechanical properties if it was designed to have a skin mainly consisting of the $\beta$ phase. Song [9] further suggested that such a skin could be formed on the surfaces of magnesium alloys by dipping the magnesium alloy...
alloys in molten aluminium. Recently, Shigematsu et al. [10] have reported the formation of such a skin or layer on AZ91D by covering magnesium specimens with aluminium powder at a temperature over 430 °C. It was noticed that the surface layer [10] mainly consisted of β phase and its hardness was much higher than that of the substrate magnesium alloy.

However, the corrosion resistance of the coating [10] has not been evaluated. In this study, an aluminum-alloyed coating was applied to an as-received AZ91D ingot and its corrosion performance was evaluated to verify the expectation on the improvement of corrosion resistance.

2. Experimental

An as-received commercial magnesium alloy AZ91D ingot (8.37 wt.% Al, 0.78 wt.% Zn, 0.22 wt.% Mn, <0.005 wt.% other elements) was cut into 1×3×5 cm coupons and polished using up to 1000# SiC paper. The coupons were washed with demineralised water and acetone, and then dried. In the same time, Al powder whose purity was 99.5% was mixed with a small amount of pure ethylene glycol. After mixing, the Al powder became a paste-like glue and was painted on the specimen surfaces. It is believed that the paste-like Al powder painting should have better contact with the AZ91D substrate than dry Al powder. The painted samples were buried in dry Al powder and heat-treated in a furnace (in air with protective gas) at 420 °C for 1.5 h. Magnesium is inert to pure ethylene glycol [11]. The latter vaporized and disappeared from the Al powder after the specimen was heated above 200 °C in the furnace. After the heat-treated specimens were taken out of the furnace and cooled down in air, the remaining aluminium powder on the specimen surfaces was removed with a metal brush. The specimen surfaces were then cleaned with demineralised water and then dried.

At least 3 specimens with the Al-alloyed coating in parallel were used for the immersion and salt spray tests in this study. In the immersion test, the specimens were submerged in 5% NaCl solution in 500 ml beakers at 25 °C. The surfaces of the specimens immersed in the bakers were observed by the naked eye in situ every 2 h in the day time (no observation was conducted during the night time). As the naked eye observation is not very sensitive, more frequent observations cannot significantly improve the accuracy of this experiment. The salt spray test was conducted in a salt spray chamber (Vostech VSC450) according to ASTM B117 standard (i.e., in 5 wt.% NaCl salt fog at 35 °C). Salt spraying had to be stopped for about 2 minutes in every 2 h to observe the changes of the specimen surfaces by the naked eye. The short pause in salt spraying could not significantly change the thickness of the deposited salt solution film on the specimen surfaces and would not affect the corrosion of these specimens. The first visible pitting occurring observed by the naked eye under immersion or salt spray condition was noted as an indicator of the breakdown of the coating. For a better understanding of the corrosion performance of the coating, uncoated specimens were, i.e., as-received AZ91D coupons, also tested in the same way for a comparison purpose.

Polarisation curves and electrochemical impedance spectra of the coated and uncoated specimens were also measured in 5 wt.% NaCl solution at 25 °C by using a Solatron 1287+1255B electrochemical measurement system. A specimen was first immersed in the NaCl solution for about 5 min, then AC impedance measurement was carried out at the corrosion potential of the specimen. Polarisation curve was then measured immediately after the AC impedance measurement finished. The amplitude of applied AC signal was 5 mV and the measured frequency range was from 1 mHz to 1 kHz. For a quick comparison of the polarisation behaviors of the coated and uncoated specimens, a scanning rate of 10 mV/min was used in the measurements of the potentiodynamic polarisation curves. The reference electrode used in these electrochemical measurements was a silver/silver chloride electrode and the counter electrode was platinum net.

The phase constituents of the coating were determined by a Bruker AXS D8 X-ray system using a cobalt target operated at 40 eV. In addition, the measurement of micro-hardness was conducted on the cross-section of a coated coupon under a load of 15 g. The loading time was 30 s.

3. Results and discussion

3.1. Corrosion resistance

The salt spray and immersion results are listed in Table 1. The as-received AZ91D suffered from severe localised corrosion after exposure to salt fog or immersed in salt solution for less than 2 h. For the specimens with the Al-alloyed coating applied at 420 °C, the first pitting appeared after exposure to salt fog or solution for 48–72 h. Even after 30 days of immersion in the 5% NaCl, there were only a few pits on the coating and the pitting areas were still small. This suggests that the coating significantly enhanced the corrosion resistance of AZ91D.

The above difference in the corrosion resistance between the coated and the uncoated AZ91D can be further confirmed by the AC impedance measurements (see Fig. 1).

<table>
<thead>
<tr>
<th>Coating</th>
<th>As-received AZ91D (no coating)</th>
<th>Al-alloyed coating at 420 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion test</td>
<td>Salt spray</td>
<td>Immersion</td>
</tr>
<tr>
<td>Time to the first observed pitting</td>
<td>1–2 h</td>
<td>48–72 h</td>
</tr>
<tr>
<td></td>
<td>2 h</td>
<td>48–96 h</td>
</tr>
</tbody>
</table>

Table 1

Pitting corrosion of uncoated and coated AZ91D specimens exposed to 5 wt.% NaCl fog and solution
The diameter of a capacitive loop in the Nyquist plane represents the polarisation resistance of the electrode. A greater polarisation resistance normally means a lower corrosion rate. In Fig. 1, the capacitive loop for the coated AZ91D alloy is much larger than that of the uncoated alloy, which signifies that the corrosion rate of the coating is much lower than that of the as-received AZ91D. This is in good agreement with the corrosion results listed in Table 1 and confirms the enhancement of corrosion resistance of the alloy by this coating.

3.2. Effect of temperature

It was found that the AZ91D specimens after being painted, buried in Al powder and heat-treated at different temperatures had different surface colors. When the heat-treatment temperature was lower than 400 °C, the specimen surface was dark. If the specimen was heat-treated at a temperature above 400 °C, its surface was relatively bright. After examining the cross-sections of the specimens under a microscope, it was found that the different surface colours after heat-treatment actually indicated whether a coating had formed on the surface of the specimen or not. No coating was formed if the surface became darker after the heat-treatment. In this case, the dark surface had a similar appearance to the surface of AZ91D being simply heat-treated in air without Al painting and Al powder. If a coating had been formed on the specimen surface, the surface normally was relatively bright.

The corrosion resistance of the coating formed at different temperatures is compared in Table 2. It seems to be impossible to obtain a continuous coating if the heat-treatment temperature is lower than 400 °C. Only at temperatures above 400 °C, can a corrosion resistant coating be formed on the AZ91D specimen.

3.3. Coating characteristics

Two typical cross-sections of the coating formed at 420 °C are presented in Fig. 2. The microstructures of the coating are characterized by the following features: 1) The coating mainly consists of small equi-axed grains and dendrites, which can be more clearly seen in Fig. 2(b). 2) The coating appears to be able to penetrate deeply into the substrate along its grain boundaries (see Fig. 2(a)). The penetrated coating is different from the originally existing β phase in morphology. The difference will be further illustrated latter. 3) The thickness of the coating varies considerably over the specimen surface, ranging from 10 μm to 200 μm as shown in Fig. 2(a) and (b).

The phase constituents of the coating were determined by X-ray diffraction (XRD) (see Fig. 3). Intermetallic Mg17Al12 (β phase) and Mg can be easily identified in the spectrum. This means that the β phase is a main component of the coating.

3.4. Corrosion protection mechanism

Since the coating is rich in β phase (Fig. 3), improved corrosion resistance by this coating can be expected. It has been well documented that a high volume fraction of β phase can act as a corrosion barrier and significantly reduce the corrosion rate [4–6]. The polarisation curves (see Fig. 4) further illustrate the reason for the increased corrosion resistance. The anodic current density is much lower for the Al-alloyed coating than for AZ91D. This means that the coating is much more corrosion resistant than the substrate.

Another important characteristic displayed on the polarisation curves is that the coating has a more positive corrosion potential than AZ91D. It is well known that the corrosion potential of β phase is always much more positive than that of AZ91D [4–6]. Therefore, the relatively positive

<table>
<thead>
<tr>
<th>Coating temperature (°C)</th>
<th>Coating formation</th>
<th>Time to the observed first pitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>No visible coating</td>
<td>2 h</td>
</tr>
<tr>
<td>300</td>
<td>No visible coating</td>
<td>8 h&lt;24 h</td>
</tr>
<tr>
<td>360</td>
<td>No obvious coating</td>
<td>8 h&lt;24 h</td>
</tr>
<tr>
<td>400</td>
<td>Non-uniform coating</td>
<td>48–72 h</td>
</tr>
<tr>
<td>410</td>
<td>Uniform coating</td>
<td>48–96 h</td>
</tr>
<tr>
<td>420</td>
<td>Coating and some local melting characteristic</td>
<td></td>
</tr>
</tbody>
</table>

* The specimens were immersed in 5 wt.% NaCl at 8:00 am. No pitting was observed until 8:00 pm. No observation was made after that. Next day at 8:00 am the pitting corrosion had occurred on the surfaces of all these specimens.
potential is consistent with the optical observation and the X-ray result that the major constituent of the coating is β phase and the high volume of the β phase in the coating is responsible for the high corrosion resistance of the coating. Even though the cathodic polarisation curves in the figure were measured in a relatively narrow range, the tendencies of the cathodic polarisation behaviours of the coated and uncoated specimens can be compared. It seems that the cathodic current density of the Al-alloyed coating tends to be slightly higher than that of AZ91D. The different tendencies are consistent with the different polarisation curves of AZ91 and β phase [12], which further confirms that the Al-alloyed coating is rich in β phase.

The Al-alloyed coating cannot be defect-free. For example, the thickness of the coating is not uniform. It is thick in some areas but very thin in some other areas (see Fig. 2(a) and (b)). There could also possibly be some pinholes in the coating due to imperfect contact of Al powder with the AZ91D substrate in some local areas. Pitting corrosion should preferentially initiate at these defects (pinholes and very thin areas) in the coating.

For a normal coating, if it is broken somewhere, severe corrosion of the substrate will occur in that location. The polarisation curves for Al-alloyed coating and AZ91D substrate (Fig. 4) also suggest that if the Al-alloyed coating is broken or some pinholes are initially formed in some local areas, the coating adjacent to these defects will act as cathode and the exposed substrate AZ91D will be severely corroded due to the galvanic effect between them.

However, the experimental results in this study showed that the pitting corrosion of coated AZ91D developed very slowly. Fig. 5 presents the corrosion morphologies of uncoated and coated specimens. The corrosion had penetrated to a considerable depth in the uncoated AZ91D substrate after the specimen was immersed in 5% NaCl solution for only 1 day. In contrast, the corroded area on the coated specimen was relatively shallow in the broken area (or defect) of the coating after immersion. It penetrated to a similar depth after 20 days of immersion.

By carefully examining these photos, it can be found (see Fig. 5(a)) that the β phase is actually intact in the corroded areas of uncoated AZ91D and corrosion was stopped by this phase in some cases. In some other areas,
corrosion actually stopped in the α matrix where the Al solute is normally relatively high before reaching the β phase. Corrosion being stopped by β phases and the Al-rich zones in the α matrix have also been reported elsewhere [13,14]. Therefore, the result actually suggests that the corrosion resistance of the substrate can be further improved by the presence of more continuous β phase in the grain boundaries and more Al-rich zones in the α matrix.

A probable explanation for the shallow pitting on the coated specimen could be that the AZ91D substrate underneath the Al-alloyed coating is different from conventional AZ91D without coating. During the formation of the coating at 420 °C, the intergranular regions of the substrate could be melted to some degree, so Al from the Al painting and Al powder penetrated relatively easily into the substrate along some grain boundaries and formed more continuous β phase there (see Fig. 5(a)). In the same time, aluminum also diffused into the α matrix of the substrate from the coating, leading to higher aluminum content in the α matrix and more continuous Al-rich zones along the grain boundaries. Therefore, apparently the coating process resulted in a clear surface layer rich in β phase on the top of AZ91D substrate. In fact, hidden underneath the apparent coating there could be another continuous high aluminium layer in the α phase with more continuous β phases along the grain boundaries in the substrate.

Since β phase is almost inert and an Al-rich zone in the α matrix is much more corrosion resistant than an Al-depleted zone [13,14], the more continuous β phase and Al-rich zone along the grain boundary can more effectively stop corrosion penetrating from grain to grain in the substrate under a broken coating. Moreover, with the Al-rich zone in the α matrix of the substrate underneath the coating, the galvanic corrosion caused by the coating at the broken area should become less severe. A good example for illustrating the reduced galvanic corrosion by the Al-rich zones in the α matrix is the corrosion morphology of AZ91E published earlier [15,16]. The β phase along the α grain boundaries is an effective cathode. Theoretically, the α grain boundaries should be preferentially corroded due to the galvanic effect of the β phase. However, due to high Al content in the α phase grain boundaries, these boundaries were actually not corroded. Instead, central areas of the α grains where are relatively depleted in Al solute were preferentially corroded in spite of the much stronger galvanic effect by the β phase along the grain boundaries [15,16]. The corrosion at the broken areas of the coating is similar to this example as the Al enriched α phase layer in contact with the coating rich in β phase. In this case, the galvanic effect should be relatively weak at the broken areas of the coating due to the continuous Al enriched layer in the substrate underneath the coating. Therefore, the substrate underneath the coating could be more corrosion resistant than conventional AZ91D in terms of general corrosion and galvanic corrosion and the pitting developed more slowly after the coating was broken (Fig. 5).

3.5. Influence of coating on other properties

Hardness is an indicator for wear resistance which is also one of the important properties of a coating in practice. The low hardness (HV60–80) of AZ91D, together with its unsatisfactory corrosion resistance, has limited the practical applications of AZ91D. It is desired that a coating cannot only improve the corrosion resistance but also have a beneficial contribution to the surface hardness.

![Fig. 5. Cross-sections of corroded areas of (a) AZ91D immersed in 5% NaCl for 1 day and (b) coated AZ91D immersed in 5% NaCl for 20 days.](image)

![Fig. 6. Schematic diagram for the distribution of hardness across the coating.](image)
For an accurate measurement of the micro-hardness of the coating, a relatively thick section of the coating was selected. Fig. 6 shows the change in microhardness across the Al-alloyed coating. In this diagram, letters "a"–"e" indicate the relative locations on the cross-section where the micro-hardness was measured. It can be seen that the micro-hardness in the substrate is only 68.3–77.1 HV while it ranges from 193 to 235 HV in the coating, which is even slightly higher than that of the coating by Shigematsu et al. [10]. The high microhardness of this coating compared with the substrate AZ91D can be attributed to the larger volume fraction of $\beta$ phase in the coating, because $\beta$ phase is much harder than $\alpha$ phase.

In addition to the corrosion resistance and wear resistance, there are still many other mechanical properties critical to the use of magnesium alloys in practice. These properties are mainly determined by the microstructure and composition of the alloy. Ideally, the formation of a coating on an alloy should not significantly change the microstructure and composition of the substrate alloy and hence not lead to deterioration of the properties of this alloy.

During the coating process, the surface of the alloy was exposed to Al powder and could change in the composition. However, the bulk of the alloy was not affected by Al powder. In order to investigate the influence of the coating process on the bulk microstructure of the AZ91D substrate, an AZ91 specimen was heated at 420 °C in a furnace for 1.5 h and then cooled down in air outside the furnace. This specimen should experience the same heat-treatment history as the bulk of a specimen with Al powder on its surface. The microstructures of this heat-treated specimen and an as-received AZ91D specimen are compared in Fig. 7. There are many $\beta$ phase precipitates in the as-received AZ91D (Fig. 7(a)). The heat-treatment did not change the basic feature of the microstructure of the substrate, particularly the distribution of the $\beta$ phase (Fig. 7(b)). It should be stressed that the $\beta$ phase is relatively short and dull in shape, different from the $\beta$ phase resulting from the penetration of coating along the grain boundaries (Fig. 2(a)) which is more continuous. The different morphologies of the $\beta$ phases (Fig. 7) and (Fig. 2(a)) confirm the contribution of the coating process to the intergranular phase in the substrate underneath the coating as discussed earlier. More importantly, it is noticed that the heat-treatment resulted in some relatively dark areas in the $\alpha$ matrix next to the $\beta$ phases (Fig. 7(b)). Optical observation at a higher magnitude in the laboratory revealed that some very fine discontinuous $\beta$ precipitates could be formed in these dark areas after the heat-treatment. These dark areas next to the continuous $\beta$ precipitates originally had a much higher Al solute level than the bright areas before heat-treatment (Fig. 7). The precipitation of the discontinuous $\beta$ phase in some Al-rich zones in the $\alpha$ matrix probably occurred while the specimen was cooled down in air after the heat-treatment. Fortunately, this kind of precipitation is beneficial to the mechanical properties of the alloy [17]. Therefore, the developed coating technique actually significantly improves the corrosion and wear resistance of AZ91D without scarifying its mechanical properties. This is of great significance in terms of the practical application of the coating.

4. Summary

An Al-alloyed coating can be formed on AZ91D magnesium alloy covered by aluminium powder at 420 °C for 1.5 h. The coating is rich in $\beta$ phase and is much more corrosion resistant and harder than AZ91D. The improved corrosion resistance verifies the hypothesis [9] that the corrosion performance of a magnesium alloy can be enhanced by a “skin” rich in $\beta$ phase.

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