Influence of spraying time on corrosion behavior of plasma sprayed alumina coatings on AZ31B magnesium alloy under salt fog environment

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Received 18 January 2016; accepted 28 July 2017

Effect of spraying time on the corrosion behaviour of uncoated and atmospheric plasma sprayed alumina (APS) coatings on AZ31B magnesium alloy in NaCl solutions of different spraying times, viz., 1 h, 4.5 h and 8 h has been examined. The corroded area was characterized by an optical microscope and X-ray diffraction. The results showed that the corrosion destruction of uncoated and coated samples was considerably affected by spraying time. The uncoated magnesium and alumina coatings were found to provide a better corrosion resistance in lower spraying time (1 h). However, the coatings and Mg alloy substrate were identified to be highly susceptible to localized damage, and could not provide an effective corrosion protection in higher spraying time (8 h). It was observed that the corrosion resistance of the ceramic coatings and base metal gets deteriorated with increasing the spraying times.

Keywords: Atmospheric plasma spraying, Magnesium alloy, Spraying time, Corrosion, NaCl

Increasingly more attention has been paid to magnesium alloys because of their low density, excellent casting performance, high specific stiffness and the ability to be recycled. Consequently, magnesium alloys have been widely used in automotive, aerospace and other sectors1,2. On the other hand, a critical limitation for the broad utilization of magnesium alloys is their higher susceptibility to corrosion, particularly in aggressive environments, which is primarily related to the large chemical activity of magnesium and the unstable passive film on the surface of these alloys3,4. Several researchers have addressed the effect of numerous corrosive environments on the corrosion behaviour of magnesium alloys for the understanding of environmental variables controlling corrosion5.

Surface coating technology is one of the most reliable methods to protect the Mg alloys towards corrosion. Different coating processes are explained in the literature for protection of Mg alloys, for instance electro/electroless plating6,7, anodizing8,9, chemical conversion coatings10,11, gas-phase deposition12, laser surface alloying/cladding13 and organic coatings14,15. These methods were examined in detail by Gray and Luan16. One of them, atmospheric plasma spraying (APS) has been most commercially utilized on Mg and Mg alloys. From the APS process a comparatively thick, dense and hard oxide coating can be deposited on the surface of magnesium alloys to enhance their corrosion resistance incredibly17,18.

Altun et al.19 analyzed the effect of chloride ion concentration and pH on the corrosion and electrochemical behaviour of AZ63 magnesium alloy. Their results showed that, the corrosion rate usually increased with the decrease in pH and the increase in chloride ion concentration. Dhanapal et al.20 explored the corrosion resistance of AZ61A magnesium alloy welds in the alkaline solution is superior than that in the acidic and neutral solutions, moreover, low corrosion rate is observed at low concentrated solution and longer exposure period, and the corrosion morphology is predominantly influenced by the distribution of β-phase. Liang et al.21 have researched the influence of pH on the deterioration of plasma electrolytic oxidation coated AM50 magnesium alloy in NaCl environment. Based on electrochemical impedance spectroscopy (EIS) test, they concluded that in acidic NaCl solution (pH 3), both the MgO and ZrO₂ coatings could not provide sufficient corrosion resistance to magnesium alloy substrate in longer exposures. Gu et al.22 examined the effect of chloride ion level on the corrosion behavior of MAO modified AZ31 alloy in NaCl solutions. The results of their analysis showed that the corrosion current density increased ratio and the

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charge transfer resistance reduced ratio suggested that the level of the corrosion damage of microarc oxidation coated AZ31 alloy is much higher when chloride ion concentration is greater than 5%. Gou et al. reported that the composite coating obtained at pH value of 5.2 offers optimal integrated properties, which exhibits similar corrosion resistance and ascendant wear resistance properties to the substrate.

From the literature survey, it was understood that most of the published works have focused on the effect of pH and Cl level on the corrosion performance of uncoated and MAO coated magnesium alloys in NaCl solutions. However, until now, there is not much published information on the corrosion performance of thermal sprayed ceramic coatings on magnesium alloys with different spraying times. Hence, the present investigation was carried out to study the influence of spraying time on the corrosion behavior of uncoated and plasma sprayed alumina coated AZ31B magnesium alloy under salt fog environment were assessed and discussed.

**Experimental Procedure**

The chemical structure of the AZ31B alloy, substrate material, was found by the optical emission spectroscopy technique utilized in this study are as follows (in wt%): Al 3.0, Zn 0.1, Mn 0.2 and Mg balance. The cut sectional area of AZ31B magnesium alloy (16 mm in diameter and 15 mm in thickness) was grit blasted using cabinet type grit blasting machine ahead of plasma spraying. Grit blasting was performed using corundum grits of size of 500 + 320 µm and subsequently cleaned by using acetone in an ultrasonic bath and dried. The optimized plasma spraying parameters, displayed in Table 1, were employed to deposit the coatings. In this investigation, alumina powders with size range from 45+20 µm have been deposited on grit blasted magnesium substrates. The plasma spray deposition of the alumina powders were performed using an APS 40 kW IGBT based plasmatron (model APSS-II). Coating thickness for all the deposits were kept up at 200 ± 15 µm.

The specimens were ground with 500#, 800#, 1200#, 1500# grit SiC paper cleaned with distilled water and dried through warm flowing air. The pH value of the solution was maintained at pH 7 with concentration of 0.6M. The pH value was measured using a digital pH meter. The test method contains exposing the specimens in a salt spray chamber as per ASTM B117 standards and evaluating the corrosion tested specimen with the procedure as per ASTM G1-03 (Fig. 1).

Table 1 — Optimized plasma spray parameters used to coat alumina

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>Values</th>
</tr>
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<tbody>
<tr>
<td>Power</td>
<td>kW</td>
<td>26</td>
</tr>
<tr>
<td>Primary gas flow rate</td>
<td>L/min</td>
<td>35</td>
</tr>
<tr>
<td>Stand-off distance</td>
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</tr>
<tr>
<td>Powder feed rate</td>
<td>g/min</td>
<td>25</td>
</tr>
<tr>
<td>Carrier gas flow rate</td>
<td>L/min</td>
<td>7</td>
</tr>
</tbody>
</table>

![Fig. 1 — Test set up and specimen during the salt fog test](image-url)
containing solution was sprayed as a very fine fog mist on the samples. NaCl in tapped water was pumped from a reservoir to spray nozzles. The solution was mixed with humidified compacted air at the nozzle, and this compressed air atomised the NaCl solution into a fog at the nozzle. Heaters were maintained at 35°C cabinet temperature. Inside the chamber, the samples were rotated frequently so that all samples were exposed evenly to the salt spray mist. The temperature within the chamber was maintained at a constant level. Because the spray was continuous, the samples were continuously wet and therefore uniformly subjected to corrosion. The corrosion rate of the as coated specimen was estimated by weight loss measurement. The original weight \( w_0 \) of the specimen was noted, and then the specimen was sprayed with the solution of NaCl for various spraying times of 1, 4.5 and 8 h. The corrosion products were removed by immersing the specimens for 1 min in a solution prepared using 50 g chromium trioxide (CrO3), 2.5 g silver nitrate (AgNO3) and 5 g barium nitrate \([\text{Ba(NO}_3\text{)}_2]\) for 250 mL distilled water. Finally, the specimens were cleaned with distilled water, dried and weighed again to obtain the final weight \( w_1 \). The weight loss \( w \) can be calculated using the following relation,

\[
W = w_0 - w_1 \quad \ldots (2)
\]

where \( W \) is weight loss (mg), \( A \) is surface area of the specimen (cm²), \( D \) is density of the uncoated and as coated specimen, \( T \) is corrosion time (h).

The main phases in the alumina coating were observed using X-ray diffraction (XRD), in which the angle of the incident beam was set at 2° against the sample surface. The XRD profiles were registered using Cu Kα radiation at 40 kV and 20 mA. A SEM (JSM 6400, JEOL, Tokyo, Japan) was used to analyze the surface and the cross-section morphologies of the alumina coatings. The changes of surface micrographs were noticed by an optical microscope (MEIJI, Japan; Model: ML7100).

**Results and Discussion**

**Phase and microstructure**

The feedstock exhibits fused and then crushed, which provides its characteristic angular shape as shown in Fig. 2. From Fig. 3, it is identified that the coating provides low porosity. The micro pores and the micro cracks (Fig. 3a) are observed in the coating. Good adhesion between the coating and the substrate is observed without any visible boundary from the cross-sectional morphology as seen in Fig. 3b. The alumina coating was mainly constituted of both \( \alpha \)-Al\(_2\)O\(_3\) and \( \beta \)-Al\(_2\)O\(_3\) phases as shown in Fig. 4.

**Effect of spraying time on corrosion rate**

From Fig. 5, it is observed that the corrosion rate reduced with increasing spraying time. The highest corrosion rate is observed at the spraying time of 1 h. It proves that the primary corrosion product impeded the passage of corrosion medium and provided protection for the uncoated and coated samples. In long time spraying with magnesium dissolution and hydrogen evolution, the pH value of the solution will increase.
increase, specifically basification. Basification should be propitious to the formation of passive film, which can protect the uncoated and coated samples. The insoluble corrosion products on the surface of the alloy could slow down the corrosion rate.

With lower spraying times, a little amount of corrosion pits were observed on the surface of the material as shown in Figs 6 and 7a. At the higher spraying times, trench-like cavities appear on the surface of AZ31 specimen (Figs 6 and 7c). It is clear from the Fig. 7, localized corrosion associated with dense pitted areas showing lot of cracks on the surface of corrosion film for all the specimens tested. During
the experiment, some black areas appeared initially, these areas become larger and other similar regions appear with the increase in time. It was characterized by the observation of localized attack and several upheavals with pitting occurrence. In this case, β phase particles cannot be easily destroyed and, with the increase of spraying time, the quantity of β phases in the exposed surface would improve and finally play the role of corrosion barrier. On the other hand, there are some grains of α phase still becoming corroded, majority of the remaining α phase grains are protected underneath the β phase barrier, so the corrosion rate decreases with the increase in the spraying time which is manifestly shown in the Fig. 8b. The EDAX result shows lesser oxygenated peaks and greater peaks of aluminium as can be seen in Fig. 8c. The peak of aluminium reveals the presence of an underlined β-phase (Mg₃₇Al₁₂). This confirms that the enhancement of corrosion takes place during the early stage of corrosion. In Fig. 8d, corrosion products with good adherent properties are observed on the surface. The corrosion products comprise of the hydroxide layer which resulted from the higher peak of oxygen. The hydroxide layer formed with the increase in immersion time is the dominant factor to prevent further corrosion. This is caused by corrosion products occurring over increasing fraction of the surface, which comprises of an insoluble protective layer of Mg(OH)₂. Thus, the corrosion rate decreases with increase in the spraying time. When the spraying time was decreased, the specimen showed a spalling of the corrosion products which are easily soluble.

Figure 8e reveals all the characteristic peaks originate from the metallic Mg substrate. These peaks relate to the β-phase (Mg₃₇Al₁₂) which is higher in its intensities. It symbolizes, that the protective hydroxide layer finds it hard to form during the early hours of immersion. However, the Mg (OH)₂ phase is detected in the specimen exposed for 8 h, as shown in Fig. 8f. Besides, many small peaks are present in the patterns from 10° to 30°, which could not be attributed to a single compound. They are usually related with Mg₆(CO₃)₄(OH)₂·8H₂O considering that the CO₂ naturally present concurs with the work of Wang et al.²⁹ Mg(OH)₂ is the dominant product in the corrosion zone, and it enhances the corrosion resistance.

<table>
<thead>
<tr>
<th>Spraying Times</th>
<th>AZ31B magnesium alloy</th>
<th>Alumina coatings</th>
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<tbody>
<tr>
<td>1h</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>4.5h</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>8h</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
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Fig. 7 — SEM micrographs of corroded surface after exposure in NaCl solutions of different spraying times
A surface pore can be observed in Fig. 9a (as shown by a circle). The corrosion products are visible within the pore (Fig. 9b). The EDX analysis revealed that corrosion products contain aluminium and oxygen. It seems that this pore has been plugged through corrosion products formed because of corrosion of substrate. The occurrence of uniform corrosion can be observed as shown in Fig. 10a. However, in the as-coated sample, an additional thicker top layer at discrete locations can be noted (Fig. 10a) indicative of higher corrosion rate. The main corrosion products formed are bayerite (Al(OH)₃) and aluminium oxide (AlO) as confirmed by EDX as seen in Fig. 10b.

The cross-section images of as-coated specimens revealed significant signs of degradation in the coating/substrate interface Fig. 11a evidences the extent of the corrosion process that occurs in the chloride medium, because the as-sprayed alumina coating was separated from the AZ31B substrate after
8 h of exposure. Examination of the coating/substrate interface demonstrated the presence of corrosion products in this area, although only a part of them stayed over the substrate or in the coating after the salt fog tests. This behaviour is produced because the as-sprayed coating is hugely porous, so that, there are a high number of pathways through this coating and the electrolyte quickly gets to the magnesium alloy surface, giving rise to the substrate corrosion. Afterwards, the corrosion process moves along the
interface area, providing rise to the formation of corrosion products on the metal surface, which will finally result in the detachment of the coating. The growth of corrosion products would separate the coating from the substrate and their lower mechanical properties would allow its detachment. According to EDX analysis (Fig. 11b), corrosion products rich in Mg and O were mainly found in the interface area, along with a small amount of Al and Cl. The primary corrosion products in charge for the detachment of the coatings in salt fog environment were identified as MgO (JCPDS 77-2179) (Fig. 11c).

Conclusions
Based on the results obtained in this investigation, the following conclusions can be drawn:
(i) The uncoated and alumina coated samples were found to provide an excellent corrosion resistance in lower spraying time (1 h). On microstructural evaluation, it is proved that the corrosion morphology of the alumina coatings depend mainly on the spraying time.
(ii) The corrosion rates of the uncoated substrate and alumina coatings were decreased with increasing spraying time. It resulted in the increase of hydrogen evolution with enhancing the spraying time, which tended to increase the concentration of OH⁻ ions therefore increasing fraction of the surface, which is the insoluble corrosion products. The insoluble corrosion products on the surface of the alloy could decelerate the corrosion rate.
(iii) The uncoated and plasma sprayed alumina coatings on AZ31B magnesium alloy were identified to be highly susceptible to localized damage, and could not provide an effective corrosion protection in higher spraying times. It means that the both the coatings and substrate experienced a better corrosion protection in NaCl solution than in higher spraying times.

Acknowledgements
The authors wish to thank Dr C S Ramachandran, Post Doctoral Fellow, State University of NewYork, USA for the assistance rendered during deposition of the coatings. The authors also wish to acknowledge Mr R Selvendiran, Technical Assistant, Annamalai University for his help in carrying out this investigation.

References