Microstructural characteristics and protection performances of plasma-sprayed Al₂O₃–Al composite coatings on AZ91D magnesium alloy

Abstract: Four Al₂O₃-Al composite coatings were successfully fabricated on AZ91D alloy by plasma sprayed with changing ratios of Al₂O₃ and Al mixed powders, respectively. XRD results indicate that all the composite coatings are composed of γ-Al₂O₃, α-Al₂O₃, and Al. SEM and EDS analysis find that Al₂O₃-Al composite coatings present the interlaced structures of Al and Al₂O₃ bands. VIDAS image analysis reveals that the porosities of the composite coatings are increased by adding Al₂O₃. In the composite coatings, the hardness of Al is about 62 HV and that of Al₂O₃ is up to 1380 HV. The electrochemical polarization tests testify that Al₂O₃-Al composite coatings can effectively protect AZ91D alloy from corroding in a chloride environment. The wear test results confirm that the wear resistance of Al₂O₃-Al composite coatings is markedly superior to that of AZ91D alloy. The excellent protection degrees are attributed to their particular compositions, microstructures, and properties. Moreover, the effect of Al₂O₃ contents on the microstructures and protection performances of Al₂O₃-Al composite coatings was also studied and discussed in detail.

Keywords: composite coating; corrosion resistance; microstructural characteristic; plasma spraying; wear resistance.

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1 Introduction

Magnesium alloys have been widely used in the automotive, aerospace, and electronic industries for their unique properties, such as low density, high specific strength and excellent mechanical castability [1, 2]. Unfortunately, magnesium alloys are highly susceptible to corrosion, especially in environments containing aggressive ions as chloride ions, sulfate ions, etc. Moreover, they are soft and have low wear resistance [3, 4]. These shortages are greatly restricting their wider applications. One of the most effective ways to prevent corrosion and abrasion is to fabricate adequate protection coating. All the time researches on suitable coating materials and corresponding preparation methods become the focus by researchers, who are engaged in protection works for magnesium alloys [5].

Al₂O₃ ceramic coating deposited on metallic substrates by plasma spraying have received considerable attention for good corrosion resistance and good wear resistance [6–8]. However, the single Al₂O₃ coating presents porous layer microstructures and poor intersplat bonding, which is determined by the characteristic of plasma spraying [9, 10]. Especially, it is often obtained lower bond strength between Al₂O₃ ceramic and the metallic substrate due to their biggest difference of thermal expansion coefficient, which to a great extent impedes regular services of plasma-sprayed Al₂O₃ ceramic coating on effective protection, particularly under some harsh operating conditions.

Some existing researches have shown that the ceramic metal composite material by incorporating a second metallic phase into ceramic matrices can successfully improve mechanical properties and obtain higher bond strength [11, 12]. Al, being an excellent ductility and thermal conductivity of material, is a good candidate added to prepare Al₂O₃-Al composite material for plasma spraying. By plasma spraying, Al₂O₃-Al composite coatings have been successfully deposited on different substrates, such as stainless steel, magnesium alloy and polymer [13–15]. These studies reveal that the composite coating possesses improve microstructure, mechanical properties and bond strength with the substrates. Moreover, it has been testified that plasma-sprayed Al₂O₃-Al composite coatings largely enhance the corrosion resistance and wear resistance of the substrate materials.

This paper aimed to study and analyze the anticorrosion and antiwear protection degree of plasma-sprayed
Al$_2$O$_3$-Al composite coating for AZ91D substrate. At the same time, the effects of Al$_2$O$_3$ contents on the microstructures and protection performances of the composite coatings were studied and discussed in detail.

2 Materials and methods

Commercial extruded AZ91D magnesium alloy was used as substrate for plasma spraying. The substrate was ground with abrasive paper up to 1000 grit, cleaned with acetone, and then sandblasted using 40–60 mesh corundum before plasma spraying. Commercially pure Al and α-Al$_2$O$_3$ powders were used as the feedstock materials. The particle size and shape were confirmed by scanning electron microscope, as shown in Figure 1. The size of pure Al powders was range of 50–200 μm, and that of Al$_2$O$_3$ powders was 10–50 μm. The mixed powders of Al and Al$_2$O$_3$ were deposited on the substrate by atmosphere plasma spraying equipment (Praxair3710, Danbury, CT, USA) to fabricate four Al$_2$O$_3$-Al composite coatings on AZ91D alloy. In four composite coatings, the volume percentages of Al$_2$O$_3$ are 22.4%, 35.6%, 50.0%, 67.0%, respectively. Then, these coatings with the increasing of Al$_2$O$_3$ were orderly designated as composite coating A, composite coating B, composite coating C, and composite coating D. For comparison, pure Al coating also was prepared on AZ91D. In this work, the same plasma spraying parameters were applied to produce all the coatings, as given in Table 1. The thickness of all sprayed coatings was about 250–300 μm.

The microstructures of Al$_2$O$_3$-Al composite coatings and pure Al coating were observed by S-3400 N scanning electron microscope (SEM) attached EDS. VIDAS image analysis system was adopted to examine the porosities of the coatings. The phase structures of all the coatings were identified by RIGAKU ULTIMA4 diffractometer (XRD) with Cu Kα radiation, voltage 40 KV, and current 40 mA. The electrochemical corrosion resistance of the composite coatings and pure Al coating was measured in 3.5 wt% NaCl solution by using an Ivium electrochemical system. The work electrodes were the coating samples. Pt electrode and saturated calomel electrode (SCE) were used as the counter and the reference electrode, respectively. Before the measurement, all the coating samples were immersed in NaCl solution for 30 min to reach a steady open circuit potential. Then, polarization scan was started at a scanning rate of 0.1 mV/s. Vickers microhardness was evaluated at the polished cross section of as-sprayed coatings using a FM-300 microhardness tester under the load of 50 N with a dwell time of 5 s. Dry sliding friction and wear tests were performed in a pin-on-disc mode on a wear testing machine (MWW-1A) at 20 N, one sliding velocity of 2.3 m/min, and 10 min test duration. Number 240 sandpaper was selected as the counterpart. The weight loss was measured by using an electronic balance with a precision scale of 0.0001 g. To ensure the reproducibility of the measurements, three tests were conducted under the same test conditions for AZ91D substrate and each composite coating sample.

3 Results and discussion

3.1 Phase analysis

X-ray diffraction (XRD) was performed for determining the compositions and the relative amount of the phases in the
plasma-sprayed coatings. Figure 2A shows XRD patterns of pure Al coating, and the phase is only Al as naturally expected. Figure 2B shows XRD patterns of $\text{Al}_2\text{O}_3$-Al composite coatings. It is obvious that the composite coatings are composed of $\gamma$-$\text{Al}_2\text{O}_3$, $\alpha$-$\text{Al}_2\text{O}_3$, and Al. According to XRD results, it can be concluded that $\alpha$-$\text{Al}_2\text{O}_3$ in the starting powders mostly converted into $\gamma$-$\text{Al}_2\text{O}_3$ after spraying. It is attributed that $\gamma$-$\text{Al}_2\text{O}_3$ tends to be nucleated from the melt in preference to $\alpha$-$\text{Al}_2\text{O}_3$ at the high cooling rate due to relatively lower interfacial energy between crystal and liquid [16]. Moreover, it is obvious that the $\text{Al}_2\text{O}_3$ peaks ascend and Al peaks descend with the increase of $\text{Al}_2\text{O}_3$ ratios in the composite coatings.

### Table 1  Plasma spraying parameters for pure Al and $\text{Al}_2\text{O}_3$-Al mixed powders.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arc current/A</td>
<td>700</td>
</tr>
<tr>
<td>Arc voltage/V</td>
<td>50</td>
</tr>
<tr>
<td>Primary gas (Ar)/MPa</td>
<td>0.41</td>
</tr>
<tr>
<td>Carrier gas (Ar)/MPa</td>
<td>0.17</td>
</tr>
<tr>
<td>Spraying distance/mm</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 3A shows the microstructure morphologies of plasma-sprayed pure Al coating. In Al coating, no splat structure is found, which indicates that Al powders have completely melted during plasma spraying. Molten Al droplets quickly impact the as-sprayed surface. The metallurgical reaction can occur between the latter Al splats with high temperature and the former Al splats, and the result is that the compacted structure is formed. Figure 3B–E shows the microstructures of plasma-sprayed $\text{Al}_2\text{O}_3$-Al composite coating A–D on AZ91D substrate, respectively. It can be seen that all the $\text{Al}_2\text{O}_3$-Al composite coatings present the gray and white interlaced microstructures. EDS analysis indicates that the chemical compositions of gray bands are Al, and those of white bands are Al and O, as shown in Figure 3F. Combined with the previous XRD results, it can be confirmed that the gray structure are Al and white structure are $\text{Al}_2\text{O}_3$. The Al structures in the composite coatings are also dense, and white $\text{Al}_2\text{O}_3$ structures are evidently increasing from composite coating A to composite coating D. Figure 4 gives the interface morphologies of pure Al coating and $\text{Al}_2\text{O}_3$-Al composite coatings. It can be seen that the interface of Al phase and magnesium alloy is not obvious for all the coating samples, which is attributed the good interface combination between them due to occur metallurgical reaction of Al and magnesium alloys [14]. It also can be found that more and more $\text{Al}_2\text{O}_3$ structure distributes in the interface regions with adding $\text{Al}_2\text{O}_3$ in the composite coatings, which will affect on the interface combination of the coating and substrate. In addition, some obvious pores can be observed in the composite coatings, which are related with the characteristics of plasma-spray coatings. Moreover, the pores in these $\text{Al}_2\text{O}_3$-Al composite coatings mainly formed in $\text{Al}_2\text{O}_3$ structures. VIDAS analysis results show that the porosity of pure Al coating is only 0.6%, which is corresponding to its dense microstructure. The porosities of the $\text{Al}_2\text{O}_3$-Al composite coatings are increased with increasing $\text{Al}_2\text{O}_3$ in the coatings. The porosities of the composite coating A, B, C, and D are 1.4%, 2.5%, 8.3%, and 22.4%, respectively. However, it is worth mentioning that these pores are not

![Figure 2](image)

**Figure 2** XRD diffraction patterns of (A) pure Al coating, (B) $\text{Al}_2\text{O}_3$-Al composite coatings.
continuous from the outmost surface of the coating down to AZ91D substrate.

In order to study in detail the microstructure characteristics of sprayed Al and Al$_2$O$_3$-Al composite coatings, all the coatings were carefully observed in a greater magnification. The results were that three especial morphologies were found, as presented in Figure 5. The first special morphology is that there are a few of beads both in pure Al coating and in the composite coatings, as shown in Figure 5A. The second is that tiny Al$_2$O$_3$ splats can be
observed from a magnified Al₂O₃ band in the composite coatings, and there are some obvious pores between the Al₂O₃ splats, as shown in Figure 5B. The third is that there are a spot of unshaped particles in the composite coatings, as shown in Figure 5C. According to their shapes and EDS analysis, it can be concluded that these particles are partially melted Al₂O₃.

It is well known that the plasma-sprayed microstructure is mainly related to the feedstock melting state, which is determined by the temperature distributions of the inflight particle [17]. During plasma spraying, the temperature of as-sprayed Al powders and Al₂O₃ powders is increased when they pass through the jet due to the heating effect from the plasma flame. Under normal circumstances, all the powders are fully melted because of the high temperature caused by plasma flame. When the sprayed droplets impact on the rough surface at higher velocities, splashing will occur [18]. Al powders with low melting points are completely melted, molten Al droplets impact on the sprayed surface and take place splashing. The global splash produces, that is Al beads, are formed and retained in the composite coating. From Figure 5A, it can be observed that the size of Al beads is significantly smaller than that of the initial Al particles. Comparing to...
Al, the \( \text{Al}_2\text{O}_3 \) powders have higher melting point. Although they also are completely melted after heating by plasma flame, the latter \( \text{Al}_2\text{O}_3 \) plats with high temperature cannot highly fuse with the former \( \text{Al}_2\text{O}_3 \) plats. Simultaneously, some pores are formed between \( \text{Al}_2\text{O}_3 \) plats. The result is that the tiny splat structures with some pores are observed on \( \text{Al}_2\text{O}_3 \) bands, as shown in Figure 5B.

However, it must be mentioned that the heating states of feedstock are also affected by different flight trajectories [19]. During plasma spraying, it is inevitable that a spot of sprayed powders, especially \( \text{Al}_2\text{O}_3 \) particles with high melting points, will fly off the central heating. They may only be partially melted and retained in the coatings after impacting on the substrate, as observed in Figure 5C.

### 3.3 Corrosion performance

Figure 6 presents the typical potentiodynamic polarization curves for pure Al coating and \( \text{Al}_2\text{O}_3 \)-Al composite coatings in a 3.5 wt% NaCl solution. For comparison, the polarization curve for AZ91D substrate is also given in Figure 6. The AZ91D substrate has the lowest corrosion potential (about -1.44V), and its corrosion current density is the highest up to 4.40 A/cm². On the contrary, the pure Al coating presents the highest corrosion potential (about -1.29 V) and the lowest corrosion current density (approximately 1.87 \( \times 10^{-2} \) A/cm²). Simultaneously, it can be obviously observed that all the \( \text{Al}_2\text{O}_3 \)-Al composite coatings have higher corrosion potentials and lower corrosion current densities than AZ91D substrate. The results indicate that \( \text{Al}_2\text{O}_3 \)-Al composite coatings have better corrosion protection for AZ91D. However, their protection degrees are still lower than that of sprayed pure Al coating.

The corrosion resistance of the coating mainly is attributed to its chemical compositions and microstructures. It is known that both \( \text{Al}_2\text{O}_3 \) and Al in \( \text{Al}_2\text{O}_3 \)-Al composite coatings have good corrosion resistance, and no new phases formed at the interface between \( \text{Al}_2\text{O}_3 \) and Al during plasma spraying, which is testified by the previous XRD results. Moreover, \( \text{Al}_2\text{O}_3 \) has no conductivity. So it is impossible to take place the galvanic reaction between \( \text{Al}_2\text{O}_3 \) and Al in corrosion intermediate. Furthermore, none of the pores is continuous from the outmost surface of the composite coating down to the AZ91D substrate. This is an important feature, suggesting that the coatings are impermeable to corrosive intermediate. So \( \text{Al}_2\text{O}_3 \)-Al composite coating can act as an effective barrier between the corrosive intermediate and substrate and effectively eliminate the corrosion behavior of AZ91D alloy.

By further comparing the polarization curves of four \( \text{Al}_2\text{O}_3 \)-Al composite coatings, it also can be concluded that the difference of \( \text{Al}_2\text{O}_3 \) contents has an obvious effect on the corrosion resistance of the \( \text{Al}_2\text{O}_3 \)-Al composite coatings. For the composite coatings A and B, including relatively smaller \( \text{Al}_2\text{O}_3 \), their corrosion potential and corrosion density is the same level, which illuminates that the differences of their corrosion protection are very slight. When the volume of \( \text{Al}_2\text{O}_3 \) is added to the correspondence with that of Al, the composite coating C presents highest corrosion potential and lowest corrosion density. When the volume of \( \text{Al}_2\text{O}_3 \) is increased to exceed that of Al, such as composite coating D, comparing with composite coating C its corrosion potential decreases and corrosion density increases. This means that the corrosion protection degree of composite coating D decreases. In addition, the passive regions are observed for the composite coating C and composite coating D with more \( \text{Al}_2\text{O}_3 \), and a relatively large difference value of \( E_{\text{corr}} - E_{\text{pzc}} \) (about 0.75 V) was found, indicating that the pitting of the two composite coatings has been greatly delayed. The passive behavior also was found in Spencer’s research work [20]. The variations of corrosion resistance of the composite coatings with adding \( \text{Al}_2\text{O}_3 \) should be related to the complex microstructural characteristics of \( \text{Al}_2\text{O}_3 \)-Al composite coatings, such as different \( \text{Al}_2\text{O}_3 \) content, different porosity, and so on. On the whole, the composite coating C can provide the excellent corrosion protection degree for AZ91D substrate.

### 3.4 Microhardness and tribological properties

It is difficult to measure the bulk hardness of the \( \text{Al}_2\text{O}_3 \)-Al composite coatings due to the thinner of the composite
coatings (250–300 μm) and the special Al and Al₂O₃ interlaced microstructures. So the microhardness of Al and Al₂O₃ were tested in this work, respectively. For both structures, the measurement series comprise 10 indentations. The results show that in Al₂O₃-Al composite coatings the microhardness of Al is about 62 HV, and that of Al₂O₃ is approximate to 1380 HV. But it must point out that the bulk hardness of the composite coatings also will be enhanced with the increasing of hard Al₂O₃.

The friction coefficients are plotted versus wear time for AZ91D and four Al₂O₃ composite coatings, as shown in Figure 7A. The friction curves show that the composite coatings exhibit the same behaviors. At the initial stage, the curves are fluctuant and unsteady. After 2 min, the friction coefficients become relatively flat. Finally, the friction coefficient of composite coating A fluctuates between roughly 0.585 and 0.620. That of composite coating B is between 0.530 and 0.575. The friction coefficient of composite coating C remains between 0.310 and 0.355, and that of composite coating D changes from 0.345 to 0.420. It is obvious that the friction coefficients of all Al₂O₃-Al composite coating are lower than that of AZ91D alloy (between 0.640 and 0.715). Moreover, the composite coating C presents the lowest friction coefficient. Figure 7B shows the wear loss of AZ91D substrate and Al₂O₃-Al composite coatings against 240 SiC sand paper at room temperature. The weight loss of AZ91D is about 8.500×10⁻⁴ g/mm², and those of composite A, B, C, and D are 4.006×10⁻⁴ g/mm², 2.977×10⁻⁴ g/mm², 1.812×10⁻⁴ g/mm², and 0.880×10⁻⁴ g/mm², respectively. It also can be found that the wear losses of the composite coatings are lower that of AZ91D alloy, and the weight loss is decreased with increasing of Al₂O₃ in the coatings. These results fully show that the composite coatings effectively improve the wear resistance of magnesium alloy. It is generally accepted that the wear properties of plasma-sprayed coatings depends on the microstructure and thermal–mechanical properties [21]. According to previous structure analysis, it has known that the Al₂O₃-Al composite coating presents the morphology characteristics that the Al₂O₃ band distributes in Al matrix. During the wear testing, hard Al₂O₃ band presents good antiwear effect, and soft Al makes roles as good support and buffer. Additional, Al with good thermal conductivity in the composite coating is in favor for alleviating the concentration of the tribological heat and thermal stress on the real contact area of friction pairs [22].

Simultaneously, it can be confirmed that the effect of Al₂O₃ content on the tribological properties of Al₂O₃-Al composite coatings is also obvious, according to aforementioned friction coefficient curves and wear loss results. When the volume of Al₂O₃ is less than that of Al for composite coating A, B, and C, the bulk hardness of the composite coatings is increased with adding Al₂O₃, and the wear resistance of the coatings is gradually enhanced. So the friction coefficient and wear loss of the composite coatings are both decreasing with increasing Al₂O₃ structure. When the volume of Al₂O₃ is more than that of Al, such as composite coating D, the friction coefficient has a little increase instead. It may be relate with the relatively more porosity. The porosity usually acts to degrade the wear resistance of coatings [23]. Moreover, it must mention that the marginal coating of the composite coating D samples occurs to flake off during wearing. The possible reason is that the interface combination becomes worse due to its more Al₂O₃ at interface region, as shown
in Figure 4. Another reason is ascribed that the toughness of composite coating with more hard Al₂O₃ is decreasing, which induces to brittle fracture in the margin of the composite coating. Although wear loss of composite coating D is the lowest, it is not a perfect Al₂O₃-Al composite coating for magnesium protection.

Synthetically considering all test results, it has been decided that the Al₂O₃-Al composite coating C will be attractively studied on the surface protection applications of AZ91D magnesium alloy in the further work due to its higher corrosion resistance and much excellent wear resistance.

4 Conclusions

Plasma-sprayed Al₂O₃-Al composite coatings were prepared by using different ratios of Al₂O₃ and Al mixed powders. Microstructural characteristics and protection properties of Al₂O₃-Al composite coatings were studied. The following points were found:

1. The plasma-sprayed Al₂O₃-Al composite coatings are composed of γ-Al₂O₃, α-Al₂O₃, and Al. The composite coating presents interlaced structure of Al and Al₂O₃ bands. Al bonds present the denser structures, and Al₂O₃ bands show the splot structures with some pores. In addition, a few of Al beads and partial melted Al₂O₃ particles are retained in the composite coatings.

2. The Al₂O₃-Al composite coating can offer sufficient corrosion protection for AZ91D substrate, which is related with its special microstructures and compositions. However, the protection degrees of the composite coatings are lower than that of sprayed pure Al coating. The Al₂O₃ contents in the coatings have an obvious effect on the polarization behavior of the composite coatings.

3. In the composite coatings, the hardness of Al is about 62 HV, and that of Al₂O₃ is up to 1380 HV. The wear resistance of Al₂O₃-Al composite coatings is markedly higher than that of AZ91D substrate. The improvement in antiwear property of the composite coating can be attributed to the microstructure and thermal–mechanical properties of Al₂O₃-Al composite coatings.

When the volume of Al₂O₃ is less than that of Al, the wear resistance of the composite coatings is enhanced with increasing Al₂O₃. When the volume of Al₂O₃ is higher than that of Al, the marginal of the composite coating occurs to flake off during wearing.

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References