Al diffusion coating on Mg alloy by a surface nanocrystallization enhanced CVD process

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Surface nanocrystallization by mechanical attrition was used to enhance the chemical vapor deposition process. An aluminum (Al) diffusion coating was produced on AZ91 Mg alloy surface. This process was conducted at a relatively low temperature (400 °C) for a short time of 120 min. The results indicated that a continuous and dense Mg17Al12 intermetallic coating with a thickness of ∼8 µm formed on the Mg alloy substrate. Almost no corrosion was observed after the coated samples were immersed in 3 wt % NaCl solution for 6 h, reflecting a relatively good corrosion resistance. The formation mechanism of the Al diffusion coating is discussed based on the experimental results.

Keywords: mechanical attrition; chemical vapor deposition (CVD); aluminum diffusion coating; magnesium alloy; corrosion resistance

1. Introduction

Mg alloys are regarded as the most promising structural materials due to their low density, high strength-to-weight ratio and excellent damping properties. However, their poor corrosion resistance severely limits the industrial applications of Mg alloys [1]. Surface technology, especially by coating, is an effective method to improve the corrosion resistance of Mg alloys [2].

Aluminizing of Mg alloys by the pack cementation chemical vapor deposition (CVD) process is an attractive technique due to several advantages, including the capability of treating parts with complex shape and ease of operation in industries. The aluminizing process leads to the formation of Mg–Al intermetallic compounds Mg17Al12 and/or Al3Mg2. It has been evidenced that the Mg17Al12 phase has good corrosion resistance in chloride solutions [3]. The Al-coated Mg alloy parts are easy to recycle because the Al element is a common alloying element for Mg alloys. It has also been suggested that the Al coatings were able to combine active potential with higher hydrogen overpotential in the case of galvanic corrosion for Mg alloys, leading to much less damage than other metal-based coatings [4].

Based on the above reasons, considerable research has been conducted in order to obtain an Al-enriched surface layer on Mg alloy substrates [4–10]. In order to promote
diffusion of Al into the Mg alloy substrate, the diffusion coating is normally carried out either at a high temperature above 450°C, or for a long time of more than 12 h. Such high temperatures and long time are hardly practical in industry as they result in surface melting and cracking [11]. To solve this problem, Christoglou et al. investigated the feasibility of a low temperature aluminizing process on Mg alloy, but found that the Al coatings had very low homogeneity and density [4]. Therefore, it has been a challenge to produce a continuous and dense Al diffusion coating on Mg alloys at a relatively low temperature for a short time.

Recently, He and co-workers [12–14] have developed a new mechanical attrition (MA)-enhanced pack cementation CVD process in order to synthesize Al diffusion coating at relatively low temperature for a short time. In this process, MA was provided by a vibrating generator where surface nanocrystallization and fast Al diffusion took place simultaneously, leading to the formation of good intermetallic coatings.

In this paper, the synthesis is reported of a continuous and dense Al diffusion coating on Mg alloy at a relatively low temperature (400°C) for a short time of 120 min by using a surface nanocrystallization-enhanced CVD process. The coating formation mechanism is also briefly discussed.

2. Experimental
Commercial AZ91 Mg alloy samples with the dimensions 20 × 10 × 2 mm³ were used as the substrate. The specimens were mechanically grounded using SiC paper up to a grit of 800#, and then degreased in ethanol.

The MA-enhanced CVD process was previously described in [13]. In the present work, a mixture of pure Al powders (99 wt %) and NH₄F (2 wt %) was used as the diffusion agent. The Al powders, NH₄F and Mg alloy specimens were sealed in a cylindrical container, and were then mechanically shaken at 400°C for 120 min.

The surface and cross-sectional morphologies of the Al diffused coatings were characterized by a scanning electron microscopy (SEM) with an energy-dispersive spectrooscope (EDS). In order to study the corrosion resistance of the diffusion coatings, the coated samples were immersed in 3 wt % NaCl solution for 6 h. Blank AZ91 Mg samples were also tested with the identical operations for comparison purposes.

3. Results and discussions
3.1. Characterization of the Al diffusion coating
Surface and cross-sectional morphologies of the Al diffusion coating on Mg alloy are shown in Figure 1. The surface structure of the Al diffusion coating looks fine and a little rough, and many small pores can be observed (Figure 1a). However, no cracks can be seen. Furthermore, many indents formed, as shown by the arrows in Figure 1a, which were caused by the mechanical attrition of the balls. As observed previously [13], severe plastic deformation can be produced by the mechanical attrition. In the present process, given that the substrate (Mg alloy) and Al coatings are relatively soft, we propose that severe plastic deformation led to forming the indents on the surface of Al coatings. Figure 1b, which shows the cross-sectional morphology of the Al diffusion coating, reveals a relatively continuous and dense structure ~8 μm thick. Again the surface looks rough, but the inner layer compact. No pores, spallation or gaps can be seen in the uneven interface area, indicating a good adhesion between the substrate and the coating.
Figure 1. The surface (a) and the cross-sectional (b) morphologies of Al diffusion coating on AZ91 Mg alloy.

Figure 2. The qualitative elemental analysis along Al diffusion coating on AZ91 Mg alloy.

Figure 2 shows the qualitative elemental analysis across the Al diffusion coating on Mg alloy. The line scan began from the resin (sealed for polishing samples) to the substrate. It can be clearly seen that the Al and Mg elements were relatively homogeneously distributed in the coating. A sharp change of both elements is observed in the interface area, indicating that the transition area between the substrate and the coating is narrow, which is consistent with the results of previous work [13,14]. The EDS results showed that the content of Mg and Al in the coating was 61.9 at. % and 38.1 at. %, respectively. This is consistent with the intermetallic phase of Mg$_{17}$Al$_{12}$ (59 at. % Mg, 41 at. % Al), indicating its formation on Mg alloy after MA-enhanced CVD at 400°C for 120 min [11,15].

3.2. 

Corrosion resistance of the Al diffusion coating

The corrosion resistance of the Al diffusion coating was qualitatively characterized by the immersion test. Figure 3 shows surface morphologies of the uncoated Mg alloy and the Al diffusion coating before and after immersion in 3 wt % NaCl solution for 6 h. The gray Al diffusion coating can be seen in Figure 3b1. After immersion in NaCl solution for 6 h, the blank AZ91 Mg alloy showed a seriously corroded surface, as can be seen in Figure 3a2. In contrast, almost no corrosion was observed on the coated samples, except for a very few corrosion pits (Figure 3b2), indicating that the Al diffusion coating has a relatively good corrosion resistance.
It is well known that cracks on diffusion coatings are a big problem that deteriorate their corrosion protective ability, especially for coatings on Mg where penetration of corrosive agents can lift the whole coating layer. The dense and continuous coating microstructure formed by the MA enhanced diffusion obviously played a role as a good barrier to resist liquid penetration, although the coating was only $\sim 8 \mu$m thick (Figure 1b). Most areas of the coating do not show any corrosion signs (Figure 3b2), also suggesting that the dense and continuous coating is $\text{Mg}_{17}\text{Al}_{12}$.

### 3.3. Formation mechanism of the Al diffusion coating

In the present work, mechanical attrition was applied in the traditional CVD process. Therefore, both diffusion and mechanical attrition took place at the same time in the process. The proposed mechanism is discussed below. The NH$_4$F plays a role of activator and reacted with Al donor to form gaseous aluminum halides, providing the source of Al atoms to diffuse into the Mg alloy. It is generally known that three reactions take place simultaneously as below in order to form active aluminum atoms [Al] on the surface of Mg alloy.

\[
\begin{align*}
2\text{AlF}_3 + 3\text{Mg} &= 3\text{MgF}_2 + 2[\text{Al}], \\
9\text{AlF} &= 6[\text{Al}] + \text{AlF}_3 + \text{Al}_2\text{F}_6, \\
9\text{AlF}_2 &= 3[\text{Al}] + 2\text{AlF}_3 + 2\text{Al}_2\text{F}_6.
\end{align*}
\]

When the active [Al] atoms formed, they diffused into the Mg alloy substrate immediately. At the same time, severe plastic deformation was applied onto the surface of Mg alloy by
the mechanical attrition. It was suggested that the severe plastic deformation probably led to the refinement of grain size on the substrate surface to the nanoscale, resulting in more grain boundaries. These grain boundaries can provide fast diffusion paths for the active [Al] atoms, promoting formation of the intermetallic phase. Given that the Al powders are relatively soft with good ductility, we propose that some Al powders were directly welded onto the surface of the substrate under the ‘hit’ effect of the mechanical attrition, shortening the diffusion distance of [Al] atoms. As the Mg$_{17}$Al$_{12}$ intermetallic coating was relatively brittle, the mechanical attrition possibly locally removed some parts of the coating, leading to a rough surface. These explain the formation of a dense, continuous and rough Al diffusion coating on Mg alloy, at the relatively low temperature (400°C) for a short time of 120 min (Figure 1b).

4. Conclusions
A mechanical attrition-enhanced CVD process was applied to synthesize Al diffusion coating on AZ91 Mg alloy. The process was conducted at a relatively low temperature (400°C) for a short time of 120 min. A continuous and dense Mg$_{17}$Al$_{12}$ intermetallic coating with the thickness of $\sim8$ µm was formed on the Mg alloy substrate. The coating demonstrated a good corrosion resistance in the chloride containing solution. This technique may find a wide range of industrial applications to provide protection for Mg alloys.

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