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Review

Protective diffusion coatings on magnesium alloys: A review of recent developments

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ABSTRACT

This study reviews the recent progress in preparation and properties of diffusion coatings on magnesium alloys. Surface alloying of magnesium alloys by diffusion coatings has been considered as an effective approach to providing the protection of magnesium alloys because of the following distinct potential advantages. Firstly, the diffusion coating has high adhesion strength since there is a strong metallurgical bond between the coating and the substrate. Moreover, the good electrical conductivity of the coated magnesium alloy can be maintained and thus its electromagnetic shielding property will not be lost. In addition, the alloyed layer comprises of intermetallic compounds, which can improved both the corrosion resistance and the mechanical properties. Therefore, various methods have been developed in an effort to fabricate diffusion coatings on magnesium alloys. This review begins with the basic principles and challenges of fabricating diffusion coatings on magnesium alloys. The types and principles of coating methods are next described. The processes of preparing diffusion coatings can be categorized into two groups: (i) one-step processes including pack cementation, vacuum aluminizing, chemical vapor deposition and molten salt bath; (ii) multi-step processes such as surface mechanical attrition treatment plus pack cementation and post heat treatment of the metallic coatings. Based on understanding the principle of each coating process, the varied microstructures depending on the processing methods and parameters, are highlighted. The corrosion and mechanical properties of the coatings are also discussed on the basis of literature data. In particular, the corrosion property especial the passivation behavior of the diffusion coating is strongly influenced by the processing parameters and the subsequent coating microstructure. Through the experimental results obtained by various researchers, the coating process–microstructure–property relationships are discussed. This review closes with an outlook on areas that should be addressed in the future work.

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1. Introduction

Growing concern for reducing greenhouse gas emissions and lowering fuel consumption have been major driving forces to develop lightweight materials for automotive and aerospace applications [1,2]. Magnesium (Mg) is the lightest structural metal currently available in the world and therefore it remains a promising material for such applications. Mg and its alloys have high specific strength, high damping capacities, good castability and machinability [3]. Besides, Mg alloys are considered to be promising materials in the field of electronic industries, owing to their other unique advantages such as good electrical conductivity (good electromagnetic shielding characteristics), high thermal conductivity and good recycling potential compared with engineering plastics. However, the widespread application of Mg and its alloys has been fairly limited compared to other lightweight metals (e.g., Al, Ti). One of the main reasons is their poor corrosion resistance [4]. Mg and its alloys share a thermodynamic instability that makes them highly reactive [5]. Furthermore, the oxide films formed on the Mg and its alloys, unlike Al and Ti, are much less protective [6].

Surface coating technology is one of the most effective methods to protect the Mg alloys against corrosion. Different coating processes are described in the literature for protection of Mg alloys, such as electro/electroless plating [7–9], anodizing [10–12], chemical conversion coatings [13,14], gas-phase deposition [15,16], laser surface alloying/cladding [17] and organic coatings [18,19]. These methods were reviewed in detail by Gray and Luan [20]. Among various coating techniques, recently developed diffusion coating is of great interest because of the following distinct potential advantages:

- The diffusion coating has high adhesion strength since there is a strong metallurgical bond between the coating and substrate.
- The good properties of the Mg and its alloys, such as good electrical conductivity, electromagnetic shielding property, high thermal conductivity, can be maintained by applying a metallic diffusion coating.
- The diffusion coating usually comprises of intermetallic compounds, which may improve not only the corrosion resistance but also the wear resistance.

Based on the above reasons, considerable research has been done trying to achieve diffusion coatings on Mg and its alloys. The development of protective diffusion coatings for Mg and its alloys will be reviewed. The various coating methods and processes are described and related to the resulting coating structure and properties. The characterization of these coatings, in particular their corrosion properties, is briefly discussed.

2. Basic principles and challenges

A diffusion coating process is commonly regarded as any process whereby a base metal or alloy is either (1) coated with another metal or alloy and heated to a sufficient temperature in a suitable environment, or (2) exposed to a gaseous or liquid medium containing the other metal or alloy, thus causing diffusion of the other metal or alloy into the base metal with resultant changes in the composition and properties of its surface [21]. Diffusion coating is a thermochemical process. In this process, the surface of the substrate is enriched with selected elements by diffusion at appropriate temperatures, thus altering its properties. Such elements can be supplied in solid, liquid, or gaseous states. The process may take the name (e.g., aluminizing), depending on the diffused elements. By controlling the process parameters, such as the time and temperature, the required surface concentration and depth of the element-enriched surface layer are achieved. This allows the effective enhancement of the surface properties of the base materials. Because the process is diffusion controlled, a sharp coating/substrate interface does not exist; a diffusion gradient in the substrate occurs instead. A diffusion coating process usually consists of the following main steps: (1) the formation of active coating species through chemical reactions or physical processes; (2) the adsorption of coating species on the substrate surface; (3) the interdiffusion of the deposited coating atoms and the substrate atoms driven by chemical potential gradient, resulting in the growth of the coating phase.

Al is the most commonly used alloying element for diffusion coatings on Mg and its alloys based on the following considerations. (1) The corrosion resistance of Al and its alloys is satisfactory, and the protective film of Al exhibits self-healing behavior. (2) The formed Mg–Al intermetallic compounds have high hardness and wear resistance. (3) Being a light metal, an Al-enriched coating does not significantly increase the overall density of the Mg alloys. (4) Since Al is a commonly used alloying element for the Mg alloys, the good recyclability of the overall materials can be maintained. The “pack cementation aluminizing” was probably first described by Van Aller in a US patent filed in 1911, who prepared Al diffusion coatings on Fe and Cu [22]. After heating the metals (Fe, Cu) in a powder mixture containing Al, NH_4Cl and graphite, a protective alloy of Al was formed on the surface. But it is only since 2000 that a similar cementation process has been developed for Mg alloys [23]. There are two main difficulties in producing diffusion coatings on Mg alloys. First difficulty lies in their high chemical reactivity. Mg is prone to form an oxide layer quickly. The formation of a diffusion coating requires elemental contact. Such contact points will be inhibited by oxide films on the Mg alloys. This may prevent the formation of a diffusion coating. Moreover, since the melting point temperature of Mg is low (650 °C), the diffusion coating process has to be kept at a low temperature (usually lower than 450 °C). This temperature is more than 500 °C lower than that of the conventional pack aluminizing process (900–1100 °C). As a result, the growth kinetics of the diffusion coatings are strongly restricted since the activity of the coating elements is significantly inhibited at low temperatures.

3. Application methods

3.1. One-step processes

3.1.1. Pack cementation

Pack cementation technique is the most widely used process for applying diffusion coatings on materials including Mg alloys. In this process, the substrates are placed in a sealed or vented container together with a well-mixed pack powder mixture containing the depositing elements. Coatings are formed by heat treating the substrate, which is covered with a powder mixture, at a particular temperature. Advantages of the pack cementation process include its low equipment cost, simplicity, and flexibility in dealing with complex-shaped components [24]. The coating composition and thickness vary depending on the substrate condition, process temperature, time and pack composition. Shigematsu et al. [23] have reported the formation of an Al diffusion coating with a thickness of 750 μm by covering AZ91D Mg alloys with Al powders at 450 °C for 1 h. It was found that the surface layer consisted of γ phase $Mg_{17}Al_{12}$ and δ phase Mg, and its hardness was much higher than that of the substrate Mg alloy. Zhu and Song [25] have achieved an Al-alloyed coating on the surface of AZ91D Mg alloy by a similar process carried out at 420 °C. The only difference is that the Al powder 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. The authors believed that the paste-like Al powder painting should have better contact with the substrate than dry Al powder. The diffusion coating was also found to be rich in $Mg_{17}Al_{12}$ phase, and the coated specimen was much more corrosion resistance and harder than the uncoated one. A pack cementation process with Al, Zn mixed powders has also been applied to obtain a diffusion coating on pure Mg, ZM5 Mg alloy and AZ91E alloy [26–28]. These diffusion coatings have better corrosion resistance in NaCl solution and higher hardness, which is due to the formation of Mg–Al–Zn intermetallic compounds. Moreover, Hirmke et al. [28] have found that the addition of Zn in the powder mixture significantly promotes the formation of diffusion coatings on the surface of the Mg alloy at process temperatures between 350 and 413 °C.

In an effort to lower the treatment temperature and time of the diffusion coating process, halide-activated pack cementation (HAPC) [29,30] and vacuum pack aluminizing [31,32] have also been tried. In a HAPC process, the powder pack mixture typically consists of a metallic source (e.g., Al, Zn), a halide salt activator such as NH_4Cl, $AlCl_3$ [29] and $ZnCl_2$ [30], and an inert filler (e.g., Al_2O_3) preventing the powder mixture from sintering at high temperature. The substrate is then heated to the desired temperature under an inert environment. In these conditions, the source element reacts with the activator forming a series of halide vapor species containing the depositing elements. This diffuses through the pack to the substrate surface where it decomposes, allowing the metallic element to be deposited to diffuse into the substrate. For example, by using Al powder as donor and $ZnCl_2$ as activator, Mg–Al and Mg–Zn intermetallic compounds on Mg alloys have been prepared at 427 °C [30]. The $ZnCl_2$ reacts with the Al to form $AlCl_3$ which can react with the Mg, allowing the deposition of active Al atoms. Besides, pack aluminizing of pure Mg under a vacuum environment has been investigated [31,32]. Compared with the cementation process carried out under a protective gas [23,25–27], vacuum aluminizing significantly enhances the growth kinetics of the diffusion coatings and lowers the aluminizing temperature to 400 °C [32]. According to [32], the microstructure of the coating was a hypoeutectic structure, which was composed of a large amount of $Mg_{17}Al_{12}$ intermetallic compound. The corrosion potential of the pure Mg increased from -1.250 to -0.866 V (vs. SCE) and the corrosion current density decreased from 1.3×10^{-3} to 1.0×10^{-4} A cm^{-2} in 5 wt.% NaCl solution, after vacuum aluminizing at 420 °C for 90 min [31]. Although considerable efforts have been made, reported pack cementation processes have to be carried out at a high temperature. For example, several studies have pointed out that diffusion coatings cannot be formed below 400 °C [25,30,32].

3.1.2. *Chemical vapor deposition*

Chemical vapor deposition (CVD) involves the dissociation and/or chemical reactions of gaseous reactants in a activated (heat, light, plasma) environment, followed by the formation of a stable solid product [33]. For a typical CVD process, reactant gases are delivered into a reaction chamber at a suitably determined temperature. As they pass through the reactor these gases come into contact with a heated substrate; they then react and form a solid layer deposited onto the surface of a substrate. Usually, an inert gas is used as a diluent gas. After the reactions, the exhaust gases are trapped and then condensed before being released into the atmosphere [34]. The depositing temperature, pressure, reactant gas concentration and total gas flow are the critical parameters in this process [33,34]. Advantages of this technique include deposition of refractory materials well below their melting points, and high aspect ratio holes and complex shapes can be coated. However, a major disadvantage is that CVD requires chemical precursors as the essential reactants, which can often present safety and health hazards as they can be at times extremely toxic, corrosive, flammable and explosive [34].

Various coating materials such as TiN [35], TiCN, ZrCN [36] and metallic oxide [37] have been prepared on Mg alloys by CVD. Recently, this technique has also been used to obtain Al diffusion coatings on Mg and AZ91 Mg alloys [38]. Christoglou et al. [38] evaluated the effect of different activators (NH_4Cl, NH_4I, NH_4F, I_2, NaCl, NaF, NaI, AlF_3 and $3NaF{\cdot}AlF_3$) on the deposition of Al and concluded that among them NH_4Cl and I_2 were the best activators due to the relatively high partial pressures of the formed Al halides. The formation of the Al diffusion coating involves a displacement reaction between Mg and Al halides on the surface followed by inward diffusion of Al atoms. It is worth noticing that the formed coating on a Mg specimen treated by pack bed CVD at 420 °C for 2 h with I_2 activator consists of Mg_2Al_3 intermetallic compound [38]. This is different with that obtained by the pack cementation process (i.e., $Mg_{17}Al_{12}$ intermetallic compound) [23,25,29–32], which may be due to the higher activity of the Al species in the CVD process. However, further developments are required to achieve dense coatings without through-thickness discontinuities or pores by the CVD process [38].

3.1.3. *Molten salt bath*

Recently, salt baths have also been developed for the formation of diffusion coatings by our group [39,40]. The baths contain the coating-metal halide together with a salt mix which is fused at the process temperature. In this process, Mg alloys are immersed in a bath containing a molten salt of the species to be deposited, which then diffuse into the substrate surface. It is interesting to note that the diffusion coating temperature and the formed coating structures obtained by molten salt bath are quite different than that prepared by the aforementioned pack cementation processes [23,25,29–32]. In Zhong's work, a continuous Al diffusion coating was fabricated on an AZ91D Mg alloy in NaCl–$AlCl_3$ molten salts at 300–400 °C [39]. Noticeably, the diffusion coating temperature of Mg alloys can be lowered to 300 °C, which is more than 100 °C lower than the reported aluminizing temperatures by using pack cementation process [23,25–32]. In contrast to the powder pack cementation process, active Al atoms can be formed at a much lower temperature in molten salts, which favors the lower temperature formation of the diffusion coating. Furthermore, the diffusion coating is characterized by a single continuous $Mg_{17}Al_{12}$ intermetallic layer or layered continuous $Mg_2Al_3/Mg_{17}Al_{12}$ intermetallic compounds, depending on the treatment temperature and time [39]. Such structure is also different than that obtained by pack cementation processes, which will be further discussed later. The formed continuous intermetallic compounds greatly improve the hardness and corrosion resistance of the substrate Mg alloys in NaCl solution.

3.2. *Multi-step processes*

3.2.1. *Surface mechanical attrition treatment followed by pack cementation*

It is generally accepted that the major challenge for diffusion coating treatment of Mg alloys is to lower the treatment temperature in order to avoid the negative effect on the microstructure and properties of the substrate. Recently, the surface mechanical attrition treatment (SMAT) has been developed to combine with the conventional pack cementation process to lower the diffusion coating temperature. SMAT has been proven to be able to generate a nanocrystalline surface layer of various bulk materials including Mg alloys [41]. The basic principle of SMAT is the generation of plastic deformation in the surface layer of a bulk material by means of the repeated multidirectional impact of flying balls (GCr15 steel in most cases) on the sample surface. The plastic deformation in the surface layer under the high strain rate results in a progressive refinement of coarse grains into a nanometer regime [42,43]. The atomic diffusion in nanocrystalline surface layers is significantly enhanced compared with their coarse-grained counterparts, owing to a large volume fraction of grain boundaries which results in the short circuit grain boundary diffusion [44,45]. For example, the nitriding process for pure Fe after SMAT can be achieved at a temperature as low as 300 °C, which is 200 °C lower than that of the conventional nitriding process [43]. Similarly, the treatment temperature of chromizing and aluminizing of the Fe and carbon steel can also be markedly reduced by SMAT [46–48].

Sun et al. [41] showed that a 100 μm thick nanocrystalline surface layer with an average grain size of 30 ± 5 nm was obtained in an AZ91D Mg alloy after SMAT. By introducing such a nanocrystalline surface layer, Zhang et al. and Sun et al. [49,50] recently have lowered the diffusion coating temperature of the AZ91D alloys to 380 °C. This temperature is 50 °C lower than the reported temperatures without SMAT by using similar approach [51]. Transmission electron microscopy observations indicated the formation of a large volume fraction of pearlite-like lamellar microstructure within the alloyed layer, which was identified to be γ-$Mg_{17}Al_{12}$ precipitates in Mg solid solution matrix [50]. This Al alloyed layer enhanced the wear resistance of the AZ91D alloy under the dry sliding wear condition, which was attributed to the strengthening effect of γ phase [50]. Unfortunately, a big disadvantage of this technique is that the current SMAT techniques are not suited to components with complex shapes.

3.2.2. *Post heat treatment of overlay coatings*

There has been an increasing interest in annealing the overlay metallic coatings to form diffusion coatings in recent years. This process involves at least two steps:

(1) contact of the coating metal with the base Mg alloys;
(2) heat treatment (i.e. annealing) to result in the interdiffusion of the coating materials and substrate materials, in order to form the diffusion coatings.

Various methods including physical vapor deposition (PVD) [52–54], metal spraying [55–57] and electrodeposition [58–60] can be applied to produce metallic coatings on Mg alloys. However,

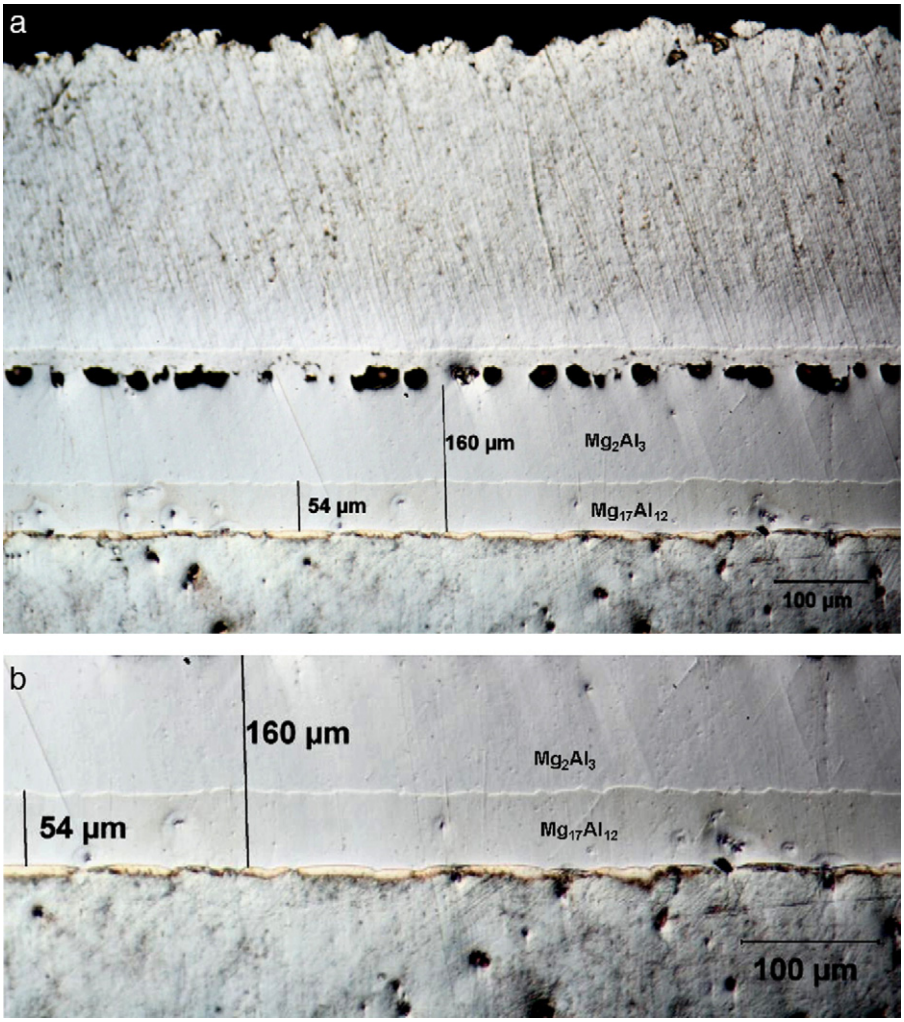

Fig. 1. (a) Typical optical micrographs showing both the Mg_2Al_3 layer and the $Mg_{17}Al_{12}$ phase layer before removing the un-reacted Al deposition (b) and after removing the Al deposition [73].

previous work has found that the adhesion strength between such overlay coatings and the substrate Mg alloy is poor, which will strongly restrict their practical applications [61,62]. Therefore, heat treatment of the overlay coatings has been tried to obtain better adhesion, owing to the formation of the metallurgical bonding provided by the diffusion coatings. Besides, annealing treatment of the coatings can also improve the hardness and wear resistance of the Mg alloys due to the formation of intermetallic compounds in the diffusion coatings. Furthermore, studies have shown that the post heat treatment is beneficial to eliminate the defects in some as-deposited coatings [63,64]. Spencer and Zhang [65] reported that cold spray of Al on AZ91 Mg substrates and subsequent heat treatment at 400 °C for 20 h produced continuous intermetallic layers ($Mg_{17}Al_{12}$ and Mg_2Al_3) at the coating/substrate interface. The thickness of the Mg_2Al_3 layer was about 150 μm and the $Mg_{17}Al_{12}$ layer was 50 μm. The electrochemical behavior of the $Mg_{17}Al_{12}$ and Mg_2Al_3 layers was similar to that of the commercially pure Al and 601 Al alloy in NaCl solution [65]. Both layers were passive over a wide potential range, suggesting that either of these intermetallic layers would have significantly better corrosion resistance in an aggressive NaCl environment than AZ91 alloy or pure Mg [65]. Heat treatment of Al coatings deposited in ionic liquid has also been tried [61,62,66]. Adhesion peel-off tests (tape tests) showed that the adhesion between the as-deposited Al coating and the AZ91D substrate was poor [62]. After heat treatment at 420 °C for 2 h, a two-phase structure coating (α-Mg + γ-$Mg_{17}Al_{12}$) with a thickness of 100–140 μm was formed, and integrated with the substrate by metallurgical boding [62]. This greatly improved the adhesion strength of the coating. Similar results have been obtained by Chuang et al. [61]. On the contrary, after heat treatment at 200–300 °C for 6–12 h, a diffusion coating with a tri-layer structure was formed on the AZ91D Mg surface [62,66]. The top layer was Al(Mg) solid solution, the mid layer was β-Mg_2Al_3 and the third layer was γ-$Mg_{17}Al_{12}$. The annealing treatment of the Al coating resulted in a significant increment of the nanohardness (3.5 ± 0.1 GPa) compared with that of the pure AZ91D alloy

Table 1
Typical results of Al diffusion coatings on Mg and its alloys collected from the literature.

Material	Coating methods	Supply of coating materials	Environment	Treatment temperature/time	Coating structure	Ref.
AZ91D	Powder pack cementation	Al powder	Protective gas	450 °C/1 h	Mg + $Mg_{17}Al_{12}$	[23]
AZ91D	Powder pack cementation	Al powder mixed with a small amount of pure ethylene glycol	Protective gas	420 °C/1.5 h	Mg + $Mg_{17}Al_{12}$	[25]
Pure Mg	Powder pack cementation	Mixture of Al, Zn powder (mass ratio: 1:1)	Protective gas	480 °C/8–24 h		[26]
ZM5	Powder pack cementation	Mixture of Al, Zn powder (mass ratio: 1:1)	Protective gas	470 °C/12 h		[27]
AZ91E	Powder pack cementation	Mixture of Al, Zn powder (0–50 wt.% Zn)		350–430 °C/3–18 h	Mg(Al, Zn) solid solution + Mg–Al–Zn intermetallic compounds	[28]
Pure Mg and AZ31	Halide-activated powder pack cementation	Mixture of Al–Si, Al_2O_3 and $AlCl_3$	Protective gas	550 °C/5–15 h		[29]
AZ91D	Halide-activated powder pack cementation	Mixture of Al, Al_2O_3 and $ZnCl_2$	Protective gas	427 °C/12 h	Mg(Al, Zn) solid solution + Mg–Al and Mg–Zn intermetallic compounds	[30]
Pure Mg	Vacuum pack cementation	Al powder	Vacuum	400–445 °C/1.5–2 h	Mg + $Mg_{17}Al_{12}$	[31,32]
Pure Mg and AZ91	Chemical vapour deposition	Mixture of Al, Al_2O_3 and NH_4Cl or I_2	Protective gas	420 °C/2 h	Mg_2Al_3	[38]
AZ91D	Molten salt bath	Molten $AlCl_3$–NaCl salt	Protective gas	300–400 °C/6–8 h	Layered continuous $Mg_{17}Al_{12}$ or $Mg_2Al_3/Mg_{17}Al_{12}$	[39,40]
AZ91D	Surface mechanical attrition treatment followed by pack cementation	Mixture of Al, Al_2O_3 and Zn	Protective gas	380–400 °C/24 h		[49,50]
AZ91D	Heat treatment of Al coating	Electrodeposited Al coating from ionic liquid	Protective gas	450 °C/10–60 min	Mg + $Mg_{17}Al_{12}$	[61]
AZ91D	Heat treatment of Al coating	Magnetron sputtered Al coating	Vacuum	450 °C/2 h	Mg + $Mg_{17}Al_{12}$	[63]
AZ91D	Heat treatment of Al coating	Electrodeposited Al coating from ionic liquid	Vacuum	200 °C/12 h 300 °C/2–18 h 420 °C/2 h	Layered continuous $Mg_2Al_3/Mg_{17}Al_{12}$ Mg + $Mg_{17}Al_{12}$	[62,66]
AZ91E	Heat treatment of Al coating	Cold spray Al coating	Protective gas	400 °C/20 h	Layered continuous $Mg_2Al_3/Mg_{17}Al_{12}$	[65]
AZ91D	Heat treatment of Al coating	Cold spray Al coating	Vacuum	400 °C/4–20 h	Layered continuous $Mg_2Al_3/Mg_{17}Al_{12}$	[76]

(1.1 ± 0.1 GPa) and the as-plated Al coating (0.7 ± 0.2 GPa) [62]. Similar work dealing with the thermal treatment of Zn/Sn plated coating on an AZ91D alloy has also been reported [67]. The heat treatment at 190 ± 10 °C for 12 h resulted in the formation of a Mg_2Sn layer, which had a better corrosion resistance than the as-plated Zn–Sn coating in NaCl solution.

Metal cladding has also been reported [68–70]. Metal sheets can be successfully bonded together under the simultaneous influence of the temperature and pressure. A diffusion coating can be formed at the interface between the metal sheets. Advantages of this process are the good density obtained and the possibility of applying thick coatings. Since this process is usually carried out at a high temperature (above 450 °C) under a high pressure, a local melting occurs during the heat treatment. The resulting microstructure of the reaction zone could contain various second phases, such as $Mg_{17}Al_{12}$ and Mg_2Al_3 [68–70].

4. Structure of the diffusion coatings

All diffusion coatings, irrespective of the coating technique, are characterized by the existence of an alloy-layer. The extent of alloying is dependent on the coating process. Part of the coating may be of the unalloyed coating metal. The microstructure and phase composition of the diffusion coating are sensitive to the processing parameters including coating methods, temperature and treatment time. To give a better understanding of the influence of the processing parameters on the coating structures, typical results for the Al diffusion coatings on Mg alloys are summarized in Table 1. Although there are many variables, it appears that the treatment temperature is the dominant factor in the microstructure of the diffusion coating. For example, the Al diffusion coatings formed at lower temperatures (200–400 °C), irrespective of the coating technique and the treatment time, are featured with layered continuous intermetallic compounds on the surface (e.g., Fig. 1) [73]. However, the higher temperature treatment (420–470 °C) always results in the formation of a two-phase structure enriched in γ-$Mg_{17}Al_{12}$ (i.e., α-Mg + γ-$Mg_{17}Al_{12}$) (e.g., Fig. 2) [62]. This is also independent of the coating methods.

Depending on the coating temperature, two simplified models for the evolution of the surface layer on Mg alloys during aluminizing can be suggested in Fig. 3. Fig. 3(a) is applicable for aluminizing temperatures below the Mg–Al eutectic reaction (437 °C) and is based on reaction diffusion rules. Firstly, the deposition of active Al atoms on the substrate surface occurs. The Al atoms absorbed at the surface then diffuse into the Mg forming Mg(Al) solid solution, driven by the chemical potential gradient (Fig. 3(a) top). This process can continue as long as the α-Mg matrix can dissolve Al at the interface between the Al medium and the substrate. As the diffusion process continues, the concentration of Al in the top surface layer keeps rising. According to Mg–Al phase diagram (Fig. 4) [71], once the Al concentration in the top surface exceeds the solid solubility of Al in Mg at a certain temperature, a reaction at the interface occurs leading to the formation of a new phase (i.e., γ-$Mg_{17}Al_{12}$, Fig. 3(a) middle). There is an Al concentration jump at the surface. Similarly, when the Al concentration at the surface becomes higher than the one acceptable in $Mg_{17}Al_{12}$, there is again a phase transformation at the surface and the formation of a second β-Mg_2Al_3 layer is observed (Fig. 3(a) bottom). As assessed by Murray [71], the γ phase $Mg_{17}Al_{12}$ has a wide composition range with Al concentration from 39.5 to 55 at.%. The β phase Mg_2Al_3 has a narrow composition range with Al content from 60 to 62.5 at.%. Data in the literature reveals that the Al concentration change in the diffusion coating is fully consistent with that referred to the Mg–Al phase diagram [71], and an example is given in Fig. 5 [76].

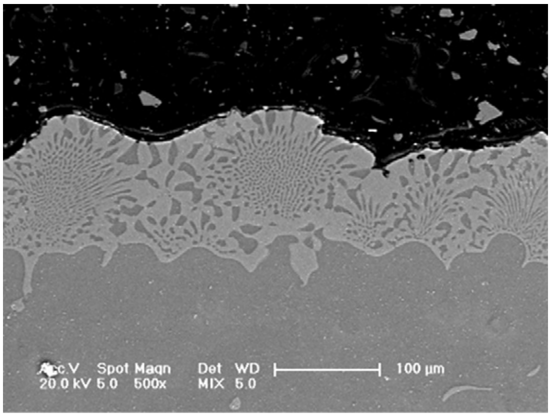

Fig. 2. Cross-section micrograph (backscatter SEM image) of Al coating on AZ91D Mg alloy after heat-treatment at 420 °C for 2 h [62].

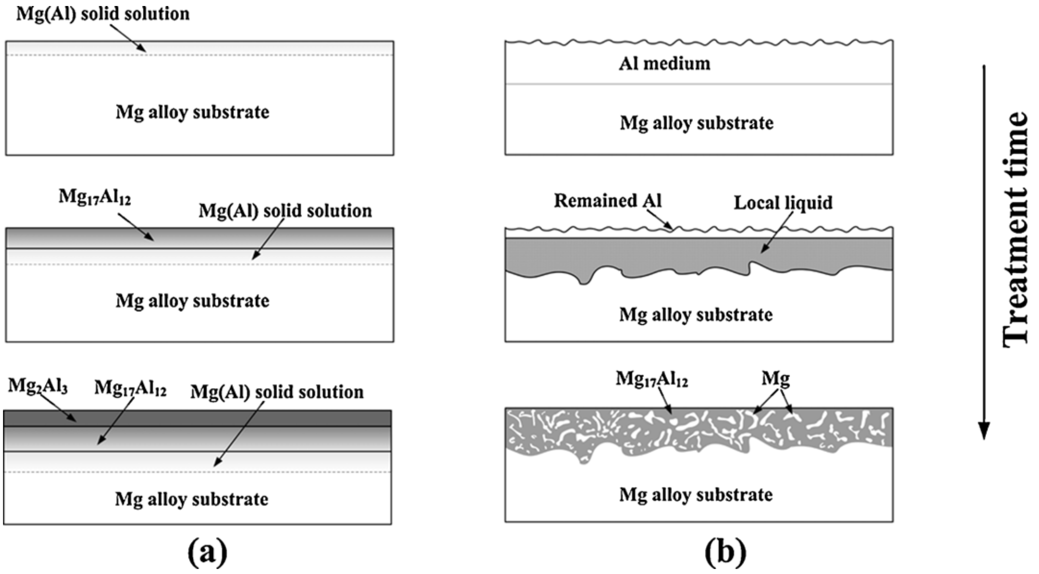

Fig. 3. Schematic diagram of the growth of the surface layers on Mg during the diffusion coating process. (a) is applicable for the lower temperature process (below 437 °C) and (b) is for the higher temperature process (near or above 437 °C).

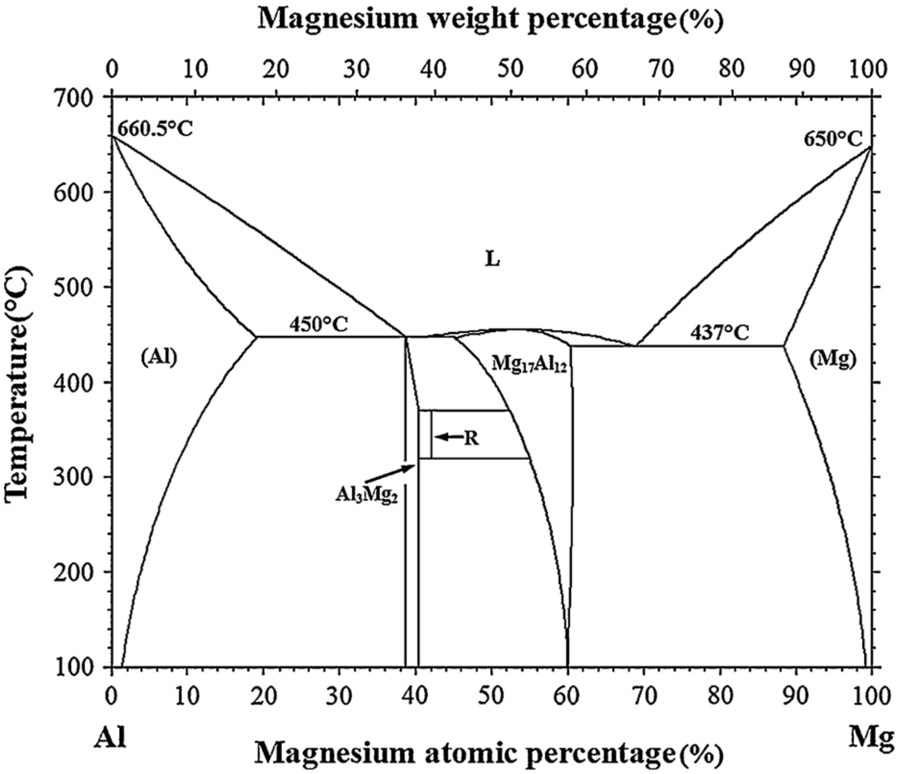

Fig. 4. Mg–Al binary phase diagrams [71].

Therefore, in this case, the composition of the diffusion coatings depends on the binary equilibrium diagram and conforms to the phase rule. The coating layers formed are thus restricted to the single-phase regions in the diagram at the process temperature and pressure [72]. However, the above discussion is not applicable to the coating treatment at a higher temperature above 420 °C. This temperature is near or higher than the Mg–Al melting point or eutectic reaction point (437 °C), and therefore Mg/$Mg_{17}Al_{12}$ eutectic reaction occurs ($L \leftrightarrow \alpha$-Mg + γ-$Mg_{17}Al_{12}$). This results in a two-phase structure or discontinuous distribution of the $Mg_{17}Al_{12}$ intermetallic phases (Fig. 3(b)).

The growth kinetics of the Al diffusion coatings on Mg and its alloys have also been investigated [29,65,66,73–76]. The results are somewhat conflicting. Some studies showed that the layer growth of the Mg–Al intermetallic phases followed parabolic law [74–76]; while other studies did not support such parabolic growth kinetics [65,66]. This may be due to the different degree of the vacancies formed in the coating caused by Kirkendall effect, which will decrease the diffusion rate. Besides, data in the literature reveals that the Mg_2Al_3 phase layer grows much faster than the $Mg_{17}Al_{12}$ phase layer [39,73–76]. A more precise Mg–Al couple study found that the growth constants of the β-Mg_2Al_3 layer increased from 7.67×10^{-10} to 3.66×10^{-9} $cm^2\,s^{-1}$ as the temperature increased from 360 to 420 °C. And the growth constants of the γ-$Mg_{17}Al_{12}$ increased from 2.13×10^{-11} to 6.06×10^{-10} $cm^2\,s^{-1}$ with the temperature increasing from 360 to 420 °C, which was about one magnitude lower than that of the Mg_2Al_3 phase [75]. Based on the Funamizu and Watanabe's founding that Al atoms diffuse more rapidly than Mg atoms [74], it is pointed out that as one of the results of the faster diffusion of Al, the intermetallic compound with a higher fraction of Al (Mg_2Al_3 phase) grows faster than the intermetallic compound rich in Mg ($Mg_{17}Al_{12}$ phase) within the diffusion coating [73]. In addition, the substrate condition can have an influence upon the growth kinetics of the diffusion coatings on Mg alloys. It was found that the growth rate of the $Mg_{17}Al_{12}$ and Mg_2Al_3 intermetallic layers on AZ91D-T4 (solution heat treatment at 400 °C for 12 h) Mg substrate were higher than that obtained on as cast Mg alloys [76]. It is believed that in the T4 state, the Al concentration is higher and more homogenously distributed within Mg matrix. Therefore the intermetallic growth is faster as less enrichment is required to reach the critical level for intermetallic formation in the substrate [76].

5. Properties

5.1. Corrosion property

The corrosion property is the surface property of the coated Mg alloys that has been studied most extensively. Mg has high chemical reactivity and low corrosion resistance. There is an increase of the corrosion resistance after diffusion coating treatment that is provided by the formation of intermetallic phases like $Mg_{17}Al_{12}$ or Mg_2Al_3 on the surface. Corrosion behavior of the Mg alloys can be characterized by accelerated methods (e.g., salt spray, immersion test), weight loss and electrochemical methods (e.g., potentiodynamic tests, electrochemical impedance spectroscopy). The actual corrosion behavior of the diffusion coating strongly depends on the processing parameters and the subsequent microstructure and coating defects. Ref. [25] studied the corrosion resistance of AZ91D before and after diffusion coating treatment in Al powders at 420 °C. It was found that the uncoated AZ91D suffered from severe corrosion after exposure to salt fog or salt solution for less than 2 h. For the specimens with the Al-alloyed coatings, the first pitting appeared after exposure increased to 48–72 h. Weight loss data has also been used to evaluate the corrosion resistance of the aluminized coating on Mg formed by vacuum pack cementation at different temperatures [32]. Weight loss curves in NaCl solution suggested that only the specimen aluminized at 420 °C had a much better corrosion resistance than the pure Mg; while the coatings obtained at 400 and 445 °C did not improve the corrosion resistance

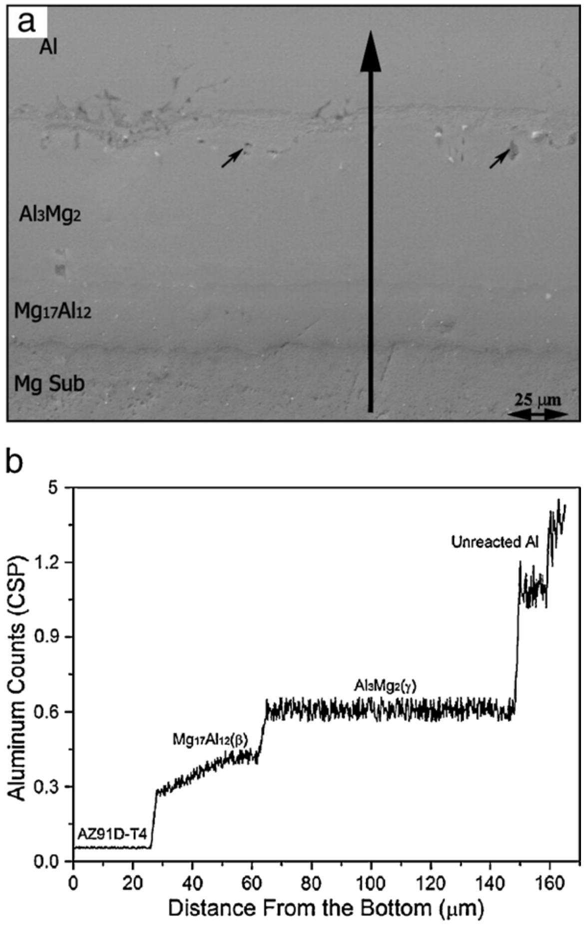

Fig. 5. (a) SEM image of cold sprayed pure Al onto AZ91D-T4 substrate after heat treatment under vacuum at 400 °C for 4 h, revealing different intermetallic phases and (b) quantitative EDS line scan as indicated by arrow in (a) [76].

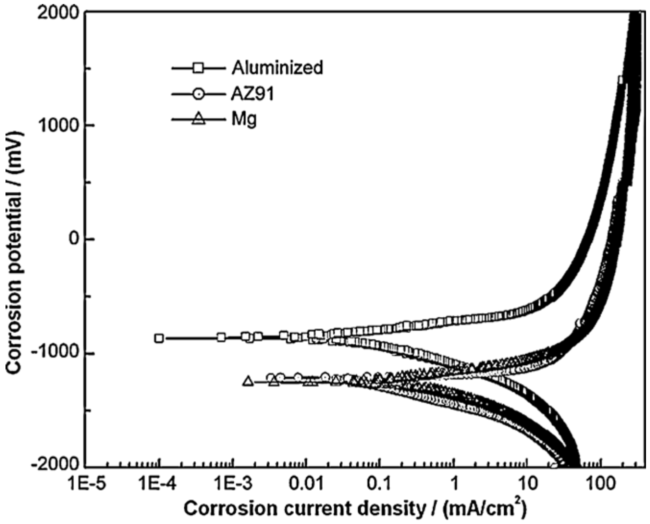

Fig. 6. Polarization curves of aluminized Mg, pure Mg and AZ91 alloy in 5 wt.% NaCl solution. Diffusion coating was formed by vacuum aluminizing at 420 °C for 1.5 h [31].

[32]. However, the detailed reason has not been given. Besides the weight loss tests, recently developed hydrogen evolution technique has been proved to be an effective method to measure the corrosion rate of Mg and its alloys. According to [77], the measurement of hydrogen evolved is equivalent to the measurement of the weight loss of Mg. By using this technique, Ref. [66] compared the corrosion performance of the electrodeposited Al coating and the Al coatings after heat treatment at different temperatures (200 °C/12 h or 420 °C/2 h). Both the as-deposited Al coating and the heat treated Al coating significantly lowered the hydrogen evolution rate in the NaCl solution, suggesting that the coatings enhanced the corrosion resistance of the AZ91D alloy. Notably, no hydrogen evolved during immersion for 72 h for the Al coated specimen treated at 200 °C for 12 h. However, some hydrogen evolution was detected for 420 °C/2 h Al coated specimen. The authors therefore concluded that the optimum heat diffusion treatment was 200 °C/12 h, for which the dissolution of Mg was significantly suppressed.

To understand the mechanistic aspects relating to the corrosion behavior of the diffusion coatings, the electrochemical tests have been conducted by various research groups. The electrochemical impedance spectrum of the bare AZ91D is featured by one capacitive loop and followed by an inductive loop in the low-frequency range in NaCl solutions. This inductive loop is related to the initial chloride-induced pit formation [78,79]. An Al diffusion coating usually results in a marked increment of the charge transfer resistance and the disappearance of the low-frequency inductive loop [40,66]. This implies that the Al diffusion coating has a higher corrosion resistance and can inhibit the spontaneous pit corrosion of the substrate. Noticeably, the polarization curves of the diffusion coatings of the Mg alloys are especially sensitive to the coating process parameters. It is possible to understand such process–property relationship by considering the microstructure change of the diffusion coating during the process. Based on the above discussion, the structure of the diffusion coatings can be briefly classified as a two-phase structure or layered continuous intermetallic compounds. The Al diffusion coatings are found to reduce the corrosion density of Mg alloys by several to several ten times, and increase the corrosion potential by 30–300 mV depending on the process parameters and the resulting structure [25,30–32,39,40,61,62,65,66,80]. A major difference between the diffusion coatings with different structures lies in the passivation behavior. For the diffusion coatings with a two-phase structure (α-Mg + γ-$Mg_{17}Al_{12}$) formed at a temperature near or above the Mg–Al eutectic temperature, there is usually no passive region in the polarization curve in NaCl solution [25–27,30–32] (see Fig. 6 for example [31]). However, a passive region can be observed for the diffusion coatings with continuous intermetallic compound layers [40,62,65,66,80] (see Fig. 7 for example [65]). This passive behavior is similar to that of pure Al and its alloys [65]. The reported extent of passive region is about 380–560 mV and the breakdown potential ranges from −0.8 to −1.1 V (vs. SCE) in NaCl solution depending on the processing parameters [40,62,65,66,80]. It is generally accepted that a passive behavior is significantly beneficial for improving the corrosion resistance. This is also confirmed by the hydrogen evolution tests [62]. By correlating the microstructure characterizations with the polarization tests, it is reasonable to assume that the distribution of the intermetallic compounds plays an important role in the passive property of the diffusion coatings. The formation of a passive film requires a homogenous distribution of the passivating element (e.g., Al). Although a two-phase structure coating enriched with $Mg_{17}Al_{12}$ phase can reduce the corrosion rate of the Mg alloys because of the barrier effect provided by the network of the intermetallic phase, such coating does not exhibit a passive behavior and cannot fully inhibit the dissolution of Mg since the inhomogenous distribution of the intermetallic compounds fails to form a passive film on the surface. On the contrary, a passive film can be formed on the continuous intermetallic compound layers. This is due to the more homogenously distributed Al element in the surface layer, which has been confirmed by SEM observations and elemental mapping (Fig. 8) [39]. Besides, the corrosion resistance

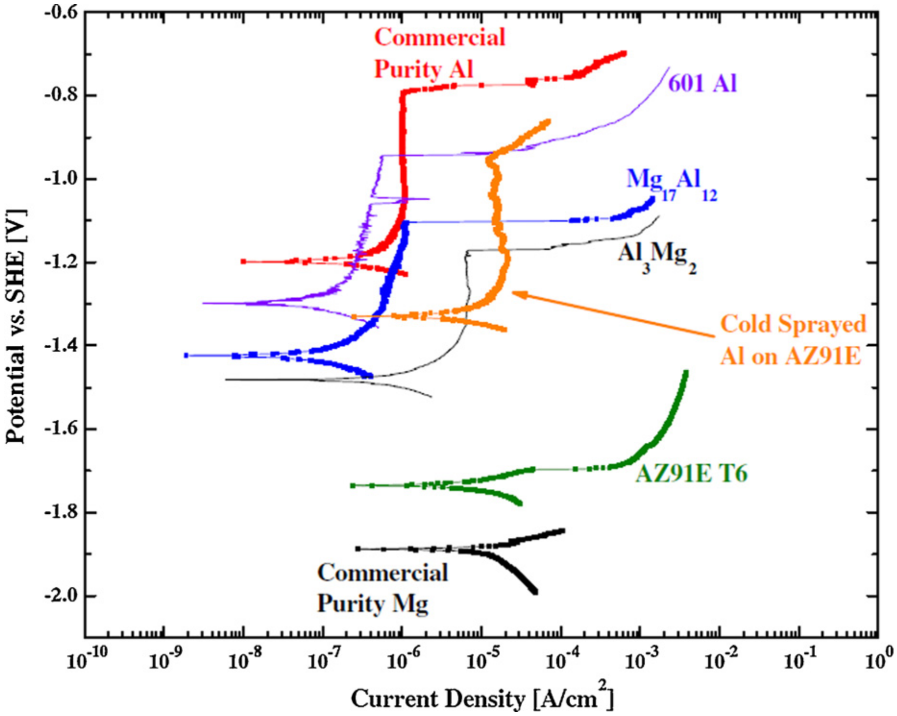

Fig. 7. Comparison of the electrochemical response of the Mg–Al intermetallic coatings with other materials, subject to linear potentiodynamic polarization in 5 wt.% NaCl; data is plotted relative to a standard hydrogen electrode potential (SHE) [65].

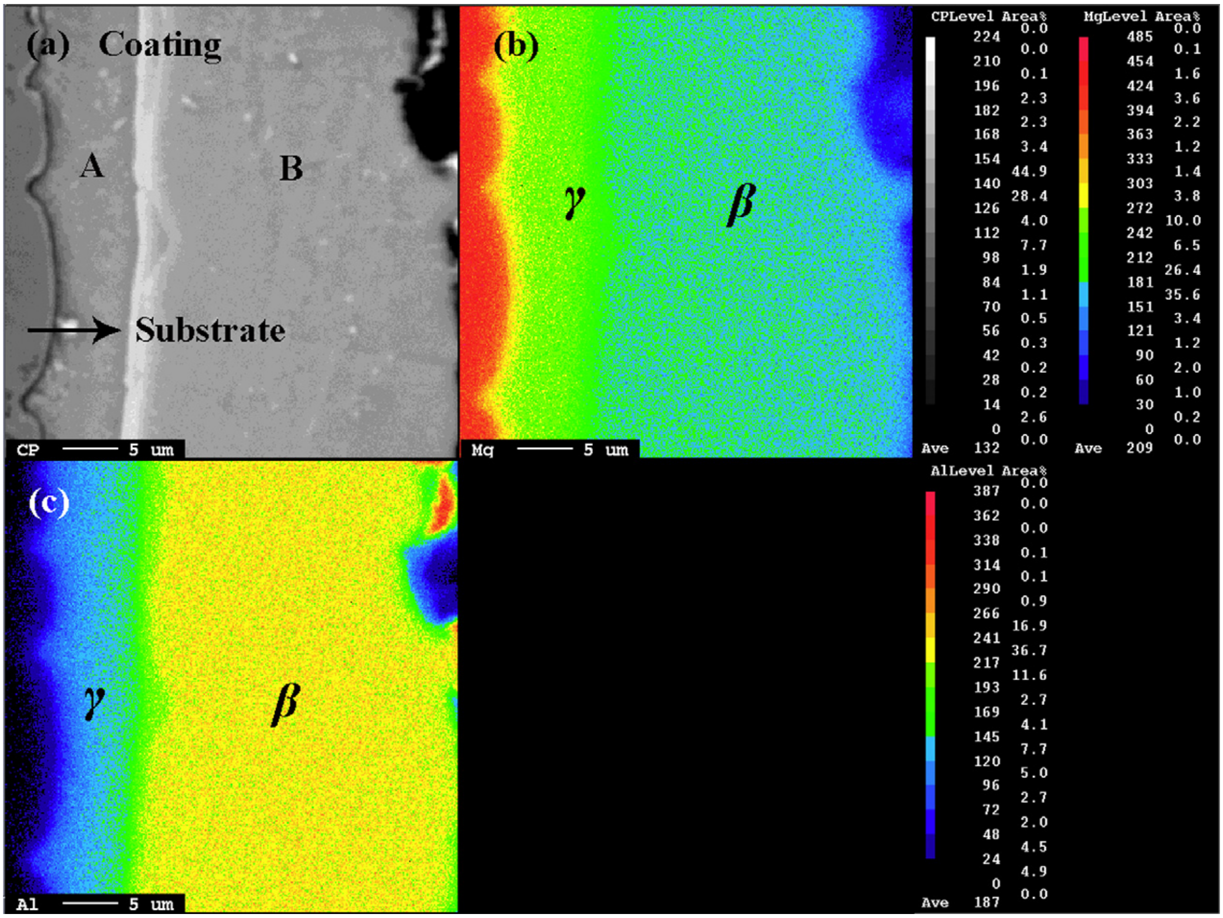

Fig. 8. Cross-sectional SEM micrographs of the (a) intermetallic coating on the AZ91D Mg alloy, EPMA-determined distribution of (b) Mg and (c) Al. The coating was formed by molten salt bath treatment at 400 °C for 6 h [39].

of the diffusion coating is very sensitive to the possible defects in the coatings. Previous work from our group studied the effect of treatment temperature and time on the corrosion resistance of the diffusion coating formed by molten salt bath [40,80]. It is found that the difference between the thermal expansion coefficient of the AZ91D substrate and the intermetallic layer may lead to cracks in the diffusion coatings, which has a negative effect on the corrosion resistance [40,80].

5.2. Hardness and wear resistance

The initial hardness of Mg and its alloys is very low (60–80 HV) depending on the chemical composition and structure of the material [23,81]. Diffusion coating treatment results in a significant enhancement of the hardness, which is due to the formation of intermetallic phases. The reported hardness of the Al diffusion coating ranges from 200 to 300 HV, depending on the processing methods and parameters [25–27,65]. The mechanical properties of Mg–Al intermetallic compounds were studied by using nanoindentation tests [73]. The continuous $Mg_{17}Al_{12}$ and Mg_2Al_3 layers were obtained by the heat treatment of a cold spray Al coating. The nanohardness of the $Mg_{17}Al_{12}$ and the Mg_2Al_3 layer is 4.35 ± 0.3 GPa and 4.40 ± 0.3 GPa respectively, which are much higher than that of the pure Mg (0.9 ± 0.05 GPa) and the AZ91D (1.24 ± 0.1 GPa). There are no cracks, pile-ups or sink-ins observed around the indent edges of the $Mg_{17}Al_{12}$ and Mg_2Al_3 intermetallic compounds. Similar results have also been reported for the diffusion coatings obtained by the molten salt bath [82]. The hardness value of the top surface of the diffusion coating is very high and it decreases to approach the hardness of the matrix in the substrate. The hardness variation along the depth of the diffusion coating to the substrate is associated with the composition changes in the coating. The wear resistance of the Al diffusion coating has also been investigated [50]. A debris abrasive wear mechanism has been found and the Al-enriched diffusion coating can effectively enhance the wear resistance of the AZ91D Mg alloys due to its high hardness [50].

6. Summary and outlook

Recent developments of diffusion coatings on Mg and its alloys have been reviewed. Evidence from the literature shows that the diffusion coatings can give a combination of high hardness and good resistance to corrosion and wear to Mg alloys, while preserving the unique properties of the Mg alloys such as the electrical and heat conductivities. Various coating methods including single processes and combined processes have been developed to fabricate diffusion coatings on Mg and its alloys. Process–structure–property relationship has been discussed. It has been found that among various processing parameters, treatment temperature plays a fundamental role in the resultant microstructures and the properties of the diffusion coatings. Diffusion coating treatment at lower temperature results in the formation of continuous intermetallic compound layers, which is based on the reaction diffusion mechanism. However, higher temperature process leads to a two-phase structure resulted from the eutectic reaction. As a result, the corrosion property especially the passivation behavior of the coatings is strongly dependent on the processing parameters and the final microstructure and composition. Electrochemical measurements reveal that the continuous intermetallic compound layers exhibit a passive behavior due to the homogenously distribution of the passivating element, but the two-phase structure diffusion coatings fail to form a passive film. The former is confirmed to have a better corrosion resistance than the latter, though both of them can enhance the corrosion resistance of the bare Mg alloy.

Although considerable developments have been achieved during the past years, diffusion coatings on Mg and its alloys are at the beginning of their development, and further investigation should be addressed in the future work. A big challenge associated with the diffusion coating is that it involves a high temperature process, which may have negative effects on the Mg alloy substrate. Therefore, the work aiming at lowering the coating treatment temperature of Mg alloys is expected to continue. This may be realized by further enhancing the activity or/and diffusivity of the coating atoms. Besides, up to date, a majority of the work has focused on simple Al diffusion coatings. Complex multicomponent diffusion coatings may be explored as a way to further increase the surface properties of the Mg alloys. More in-depth characterizations of the nature of the coatings (e.g., microstructure, composition, defects and internal stresses) responsible for affecting the surface properties are required. To study the microstructural changes and properties of the diffusion coatings, it is essential to understand the kinetics and formation mechanisms of the coatings. Furthermore, a fundamental understanding of the physical and chemical mechanisms for the failure of the diffusion coatings is still lacking. Thorough understanding and quantification of the degradation mechanisms may provide useful guidance in the development of high performance diffusion coatings and be applied to direct the practical use of such coatings.

Acknowledgments

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