

# Diffusion coatings for protection of magnesium alloys

Labdhi Gandhi, Guide's Name: Dr. Vijayshankar Dandapani

**Abstract:** This report reviews the recent development in preparation and properties of diffusion coatings on magnesium and its alloys. From among various coating techniques, diffusion coating which has recently been developed is very popular since firstly, it has high adhesion strength as there is a strong metallurgical bond between the substrate and the coating. Secondly, by applying a metallic diffusion coating, the useful properties of Mg and its alloys, such as good electrical conductivity, high thermal conductivity, electromagnetic shielding property can be preserved. Finally, it helps improve not only the corrosion resistance but also the wear resistance as the diffusion coating generally comprises of intermetallic compounds. As a result, much research has been undertaken in trying to achieve diffusion coatings on Mg and its alloys. This review begins with discussing briefly the types and principles of several common surface coating processes employed for magnesium and its alloys focusing on the basic principle for fabricating diffusion coatings on magnesium alloys. 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. We have also described the necessity of such coating mechanisms. The processes of preparing diffusion coatings can be divided into two groups: (i) single-step processes that include pack cementation, vacuum aluminizing, chemical vapor deposition and molten salt bath; (ii) multi-step processes like surface mechanical attrition treatment plus pack cementation and post heat treatment of the metallic coatings. By noting the principle of each coating process, we have also observed the varied microstructures depending on the processing methods and parameters.

## 1. INTRODUCTION

Magnesium is the lightest structural metal, about 30% lighter than aluminium, and is commonly used in alloys. Although pure magnesium burns vigorously once molten, magnesium alloys have higher melting points and are widely used in the automotive and aviation industries. Magnesium is the third most widely used metal in construction (behind iron and aluminium). Magnesium is majorly used to make alloys, that have a very low density, comparatively high strength and superior machinability. Magnesium alloys have wide variety of applications ranging from manufacturing car components such as steering wheel cores, gearbox casings, dashboard structure, radiator supports using high pressure die cast magnesium alloys, to sand-casted parts such as helicopter gearboxes and jet engine auxiliary gearboxes using magnesium alloy added with zirconium and rare earth metals. They also find use as sacrificial anodes. When attached to a less reactive metal, the magnesium acts as the anode of an electrical cell, and corrodes prior to the other metal. This is used for protecting the hulls of steel ships and the under-water structure of oil platforms and pipelines from corrosion. Magnesium is also used in distress flares, fireworks and other incendiary devices.

Although magnesium and its alloys, with one quarter of the density of steel and only two thirds that of aluminium, and a strength to weight ratio that far exceeds either, fulfils the role admirably as an 'ultra light' alloy; and a wide variety of applications can be envisaged for Mg alloys, the use at present is limited mainly due to

- (1) inferior corrosion properties, that is, Mg and its alloys prone to corrosion since magnesium has the lowest standard potential of all the engineering metals [13]
- (2) magnesium and its alloys are usually stable in basic solutions, but in neutral and acidic media they dissolve at high rates [10]
- (3) it is highly reactive due to thermodynamic instability since it loses its electrons easily compared to many metals [9,11]
- (4) less strength offered by the oxide films formed on the Mg and its alloys, unlike Al and Ti [12]

A low toxicity surface coating that enables uniform, controlled corrosion at a desired rate (this usually means it must offer barrier functions for a limited time period) is desirable [13]. That is, to guard

Mg against corrosion, surface coating technology has been proved to be one of the best methods. Various coating processes are described by Gray and Luan [14] for protection of Mg alloys against corrosion. These are described as follows:

### **1.1. Electroless plating**

Electroless nickel-phosphorus coatings are one of the favoured methods because of their enhanced corrosion-resistance properties and the coating uniformity that is achieved with complex objects. Electroless nickel is used mainly for its unusual combination of wear-resistance and corrosion properties. The coating properties are often tailored by optimizing the alloy composition, that is, providing variation within the phosphorus content within the range of 5 to 12% [15].

### **1.2. Anodizing**

Similar to plating, Mg can also be anodized to enhance its surface properties. The formation of a thick stable oxide layer on the metal's surface is known as anodizing. It is an electrolytic process in which the paint is attached with the help of the film and it also enables effective metal dyeing. The colour of the film can be thickened by introducing organic dyes or inorganic pigments. Anodization of Mg is carried out through an alkali rich aqueous bath. Utilizing direct current that may not be completely reversed in polarity or turned off during the process allows the formation of magnesium compounds in an area that has been shown to withstand good corrosion when tested with salt spray. The surface parameters like superior aesthetic appearances, and comparatively better abrasion and corrosion resistance can be obtained by adding various other elements in the aqueous bath. Anodized magnesium can easily colour and provide a good foundation for painting. However anodized oxide films provide less strength to the Mg alloys [16].

### **1.3. Chemical conversion coatings**

In this technique, the covered surface is converted into a coating with electrochemical or chemical processes. These coatings usually comprise of aluminium, vanadium, phosphate, potassium, cerium, molybdenum, zirconium, chromium, nickel, and zinc-rich layers.

The chemical conversion coating technique has been extensively utilized for application onto conventional metallic materials for corrosion protection due to the following advantages over other existing coating methods:

- This process is easy to operate, processing time is short, raw chemicals used for bath solution are cheap and no specific equipment or conditions are necessary, which is quite favoured for industrial manufacturing applications.
- This is a wet-coating technique that generates a uniformly covering layer on the surface of components comprising even of irregular shapes, like porous, hollow and screwed structures. This not possible for some line-of-sight techniques like plasma spray, RF sputtering, chemical/physical evaporation deposition, etc.
- Due to the presence of an intermediate layer between the coating and the underlying metal as well as the presence of chemical bonds, these chemical conversion coatings are more adhesive.

However, there exists one disadvantage of chemical conversion coatings and that is their relatively less durability and toughness or wear resistance capability. This results in enhanced defects and damage, which decreases the protectiveness, that severely undermines the integrity of a coating [18].

On guard magnesium alloys, usually the chemical conversion coating route is undertaken. However since ancient times as chromate causes environmental pollution, chromate conversion treatment is forbidden in numerous countries. Recently, some chromium-free conversion treatments are developed to unravel the pollution problem. To address this issue, recently chromium-free treatments like the silane technology has surfaced to provide a possible alternative to the conversion treatments containing carcinogenic chromium VI. Other chromate replacements include the usage of non-toxic pigments, such as ion-exchangeable pigments or IEPs [17].

### **1.4. Gas-phase deposition**

In magnesium alloys, corrosion reactions are originated from inhomogeneity in microstructures, like inclusions, grain boundaries and twin boundaries. These corrosion origins can be covered with a high purity magnesium layer by the gas phase deposition process resulting in improved corrosion resistance [19]. This deposition coating with high-purity magnesium of magnesium alloys is carried out using a retort method within which a purification process is intrinsically included [2-8,20]. Moreover, due to the limited solid solubility of most metals in magnesium, the improvement in the corrosion resistance of magnesium through alloying is limited. Also, alloying becomes difficult due to the

relatively high melting temperature of most of the less-common metals. Gas phase deposition is the technique in which magnesium is alloyed with nonequilibrium concentrations of incompatible metals so as to bring about an improvement in corrosion performance [21].

Another technique for protection is known as the fluoride treatment. In this the specimens of magnesium alloys are dipped into molten  $\text{NaBF}_4$  to form magnesium fluorides layers on the surfaces which shows corrosion resistance even in acidic solutions. The fluoride treatment is usually affected by the inhomogeneity present in microstructures. By combining these two processes, that is fluoride treatment and deposition coating, improved corrosion resistance can be achieved [19].

### **1.5. Laser surface alloying/cladding**

Laser cladding is a technique by which new layers of materials are deposited on a substrate by laser fusion of blown powders or pre-placed powder coatings to obtain multiple layers having shapes with complex geometry. The usage of this manufacturing process can be found for material surface property modification and repair and manufacture of three-dimensional components. This technique is capable of generating materials with desired macro or microstructures and properties [22].

Laser surface melting is a technique of localized alloy formation in which simultaneous, controlled addition of alloying elements is carried out. These alloying elements diffuse rapidly into the melt pool, and the desired depth of alloying can be obtained in a short period of time. By this process, a desired depth of alloying, alloy chemistry and microstructure can be generated on the sample surface; and the alloying elements diffuse rapidly into the melt pool. The solidification rate determines the degree of microstructural refinement. The surface of an alloy, can be selectively alloyed to enhance properties, like resistance to wear, in such a way that only the locally modified surface possesses properties typical of tribological alloys. As a result of this, a lot of cost is reduced and the dependence on strategic materials can also be limited. One method of, Either by coating a slurry suspended in organic binders or by spraying the powder mixture suspended in alcohol to form a loosely packed coating, alloying of proportionate mixtures of powders on the sample surface can be carried out [23].

### **1.6. Diffusion coating**

From among various coating techniques, diffusion coating which has recently been developed is very popular since:

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

As a result, much research has been undertaken in trying to achieve diffusion coatings on Mg and its alloys.

Diffusion coating is defined as a process in which an alloy or a base metal is either

- (1) coated with another alloy or metal and then heated to a suitable temperature, or
- (2) exhibited to a gaseous or liquid environment containing the other alloy or metal, leading to diffusion of the other alloy or metal into the base metal and changes within the composition and properties of its surface [23].

A diffusion coating process mainly consists of the following 3 steps:

- (1) formation of active coating species through physical processes or chemical reactions
- (2) adsorption of coating species on the substrate surface,
- (3) intermixing of the substrate atoms and the deposited coating atoms which leads to the growth of the coating phase and is driven by the chemical potential gradient [1].

Diffusion coating, which is a thermochemical process involves the enrichment of the surface of the substrate with certain elements by diffusion at suitable temperatures, thus changing its properties. These elements can be in the solid, liquid or gaseous states. The process is named (e.g., aluminizing), depending on the diffused elements (e.g. aluminium in this case). By controlling the temperature and the time which are the process parameters here, the required appropriate depth of the element-enriched surface layer and surface concentration can be achieved. This enables the overall enhancement of the surface properties of Mg or its alloys (that is the base metal). A sharp interface between the coating and

surface does not exist; a diffusion gradient in the substrate occurs instead since the process is diffusion controlled.

## **2. DIFFUSION COATING PROCESSES**

### **2.1. Single-step processes**

#### **2.1.1. Pack cementation**

Pack cementation process is the most commonly used technique for applying diffusion coatings on magnesium alloys. In this process, the substrates are placed in a sealed container together with a well-mixed pack powder mixture consisting of the depositing elements. The coatings are formed by heat treating the substrate, that is covered with a powder mixture, at a suitable temperature. Benefits of the pack cementation process include its low equipment cost, ability for mass production, simplicity, and flexibility in uniformly coating complex-shaped components [24]. The thickness and coating composition vary based on the substrate condition, time, process temperature and pack composition. Also, since the pack cementation process involves diffusion coatings via activator gases and, is carried out in a dry environment, the process can circumvent water related contamination [25].

The requirements of a high temperature annealing process for pack cementation coatings prevents from the practical application of the coating process on magnesium alloys, as the melting temperature of magnesium alloys is relatively lower so that the activator may not work at such a low temperature (below 873 K). It has been discovered that there are several activators that can be used in a low temperature environment, and several chlorides like  $\text{AlCl}_3$  or  $\text{AlCl}_2$  that have a high vapor pressure at lower temperatures. A pack cementation process with pure magnesium and a commercial AZ31 magnesium alloy can be carried out in an Al alloy powder in order to produce Al-Mg coating layers on the surface of the substrates. The activator  $\text{AlCl}_3$  is known to provide the highest gas pressure at low temperatures [25,26].

The basic principle of pack cementation, a batch vapor-phase process involves heating a closed or vented pack to a raised temperature for a certain amount of time during which a diffusional coating is produced [27]. The pack consists of four parts: the substrate or component which is to be coated, the master alloy, that is, a powder of the elements to be deposited on the surface of the substrate, a relatively inert filler powder and a halide salt activator. The master alloy, the filler, and halide activator are thoroughly mixed together, and the component to be coated is placed in this mixture in a retort [28]. When the temperature of the mixture is raised, the activator reacts to produce an environment of source elements halides that diffuse into the pack and transfer the source elements to the substrate on which the coating is formed [29].

#### **2.1.2. Chemical vapor deposition**

In this technique, magnesium or magnesium alloys are utilized as an evaporation source and also as substrates. The substrate is coated with deposited magnesium layer of high purity because this technique includes a purification process based on the retort effect [30]. Advantages of the chemical vapor deposition are as follows:

- It is not required to remove the deposited layer when the coated materials are recycled.
- Deposition of refractory materials is possible below their melting points.
- Scraps with magnesium alloys can be used for the evaporation source.
- It has high aspect ratio holes.
- The process does not consume energy consuming and is non-toxic for the environment.
- Also, the complex shapes can be coated by this technique.

However, a major disadvantage is that this technique needs chemical precursors as essential reactants, which can lead to safety and health hazards since they are at times extremely toxic, corrosive, flammable and explosive in nature [31].

Chemical vapor deposition or CVD is the dissociation or chemical reaction of gaseous reactants in an activated (heat, light, plasma) atmosphere, followed up by the formation of a stable solid product [32]. In a CVD process, as the reactant gases delivered into a chemical reaction chamber pass through the reactor at a suitable temperature, they come into contact with a heated substrate and react to form a solid layer deposition onto the surface of the substrate. Generally, an inert gas is utilized as a diluent gas. When the reactions are completed, the successive trapping and condensation of exhaust gases takes

place before they are released into the atmosphere [31]. The critical parameters involved in this process are depositing temperature, pressure, reactant gas concentration and total gas flow [31,32]. Various coating materials such as TiN [33], TiCN, ZrCN [34] and metallic oxide [35] 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 [36]. Christoglou et al. [36] concluded that for deposition of Al on Mg, among  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{I}$ ,  $\text{NH}_4\text{F}$ ,  $\text{I}_2$ ,  $\text{NaCl}$ ,  $\text{NaF}$ ,  $\text{NaI}$ ,  $\text{AlF}_3$  and  $3\text{NaF} \cdot \text{AlF}_3$ ; the best activators are  $\text{NH}_4\text{Cl}$  and  $\text{I}_2$  as they have relatively high partial pressures for the formed Al halides.

### **2.1.3. Molten salt bath**

Diffusion coatings obtained by immersion in molten salt baths are simple and cost lower than most processes. They produce high performance wear and/or corrosion resistant layers. The baths contain a salt mix fused at the process temperature along with the coating-metal halide. The coatings are formed at elevated temperatures by diffusion of metals or nonmetals into a substrate. The surface chemical composition is modified by diffusion elements to produce new phase transformations. In this process, the molten salt of the species that is to be deposited and Mg alloys are immersed in a bath. This molten salt then diffuses into the substrate surface, that is, the salt vaporizes and combines with the coating material to generate the transporting vapor species [37]. The formed coating structures obtained by molten salt bath and the diffusion coating temperature are very different than that prepared by the pack cementation processes beforehand [1]. On raising the temperature sufficiently, the coating material reacts with the salt to form a metallic halide vapor, which then contacts the surface of the parts to form the coating [38, 39]. Salt bath processes creates strong metallurgical bonds between the substrate and the diffusion layer.

It is stated in In Zhong's work, that a continuous Al diffusion coating can be made on an AZ91D Mg alloy in  $\text{NaCl}-\text{AlCl}_3$  molten salts at around 300–400 °C [40]. It is noteworthy that the diffusion coating temperature of Mg alloys can be reduced to 300 °C, which is more than 100 °C lower than that for the aluminizing temperatures by using pack cementation process.

## **2.2. Multi-step processes**

### **2.2.1. Surface mechanical attrition treatment followed by pack cementation**

Surface mechanical attrition treatment or SMAT induced plastic deformation, enables nano-crystallization at the surface, reduces the grain size and increases the volume fraction of nonequilibrium grain boundaries, leading to the accumulation of defects and dislocations at the grain boundaries and within the grains. These characteristics help to promote the diffusion [41]. Under the high strain rate, the plastic deformation in the surface layer leads to a progressive refinement of coarse grains into a nanometre regime [44].

This is a mechanical peening technique utilized to create very fine grain surfaces on a metal. When it is carried out on pure magnesium using different attrition media like zirconia [ $\text{ZrO}_2$ ], alumina [ $\text{Al}_2\text{O}_3$ ], steel balls, etc, we can observe its effect on microstructure, surface residual stress, surface composition, and corrosion. The disadvantages of this process are as follows:

- Although the SMAT process produces a refined grain structure on the surface of Mg, it results in a region of elemental contamination extending into the substrate, regardless of the media used.
- The recently developed SMAT techniques are not suitable for components having complex shapes.

This process is developed for synthesizing a nanostructured surface layer on the metallic materials so that the overall performance and properties can be improved. Surface contamination from SMAT is characterized using glow discharge optical emission spectroscopy (GDOES) [42]. Also, the SMAT can accomplish chemical heat treatment at relatively lower temperatures due to the formation of nanocrystalline [43]. Since lowering the temperature for diffusion coating treatment of Mg alloys is a big challenge, the surface mechanical attrition treatment combined with the conventional pack cementation process is utilized. In a study conducted by Sun et al. [45] revealed that when SMAT was performed on an AZ91D Mg alloy, we obtained a 100  $\mu\text{m}$  thick nanocrystalline surface layer with an average grain size of  $30 \pm 5$  nm. Zhang et al. and Sun et al. [46,47] lowered the diffusion coating temperature of the AZ91D alloys by 50 °C to around 380 °C by introducing this nanocrystalline surface layer [48].

### **2.2.2. Post heat treatment of overlay coatings**

Annealing the overlay metallic coatings to get diffusion coatings consists of the following two steps:

- bringing the coating metal in contact with the base Mg alloys and
- to form the diffusion coatings by causing the intermixing of the coating and substrate materials by performing heat treatment or annealing.

Physical vapor deposition (PVD) [49–51], metal spraying [52–54] and electrodeposition [55–57] are some of the techniques that can be utilized to produce metallic coatings on Mg alloys. However, due to poor adhesion strength between the Mg alloy substrate and these overlay coatings, practical applications are hindered [58,59]. Hence, heat treatment of the overlay coatings has been utilized due to its following distinct advantages:

1. better adhesion is obtained due to the formation of the metallurgical bonding.
2. improvement in the wear resistance and hardness of the Mg alloys by annealing as intermetallic compounds are formed in these diffusion coatings.
3. Also, it has been proved that defects in deposited coatings can be eradicated by post heat treatment [60,61].

Spencer and Zhang [62] found that continuous intermetallic layers ( $\text{Mg}_{17}\text{Al}_{12}$  and  $\text{Mg}_2\text{Al}_3$ ) at the interface between the coating and substrate can be produced by cold spraying of Al on AZ91 Mg substrates and then performing heat treatment at 400 °C for about 20 hr. The following characteristics were observed by Spencer and Zhang:

1. 50  $\mu\text{m}$  thickness of the  $\text{Mg}_{17}\text{Al}_{12}$  layer and about 150  $\mu\text{m}$  thickness of the  $\text{Mg}_2\text{Al}_3$  layer was obtained.
2. The two layers  $\text{Mg}_{17}\text{Al}_{12}$  and  $\text{Mg}_2\text{Al}_3$  were observed to have similar electrochemical behaviour to that of the commercially pure Al and 601Al alloy in NaCl solution [62].
3. It was concluded that either of these intermetallic layers would be significantly better corrosion resistant in an aggressive NaCl atmosphere than AZ91 alloy or pure Mg since both layers were found to be passive over a large range of potential [62].

Some common post heat treatments of overlay coatings performed over the years are:

- 1) Heat treatment of Al coatings deposited in ionic liquid

Adhesion peel-off tests performed after heat treatment of Al coatings deposited in ionic liquid revealed that the adhesion between the AZ91D substrate and the deposited Al coating was poor [59]. However, after forming a two-phase structure coating of  $\alpha\text{-Mg} + \gamma\text{-Mg}_{17}\text{Al}_{12}$  having a thickness of around 100–140  $\mu\text{m}$  by performing heat treatment at 420 °C for 2 hours and subsequently integrating with the substrate by metallurgical bonding, improvement in the adhesion strength of the coating is observed [59]. On heat treatment at 200–300 °C for 6–12 hours, tri-layer structured diffusion coating, namely Al(Mg) solid solution,  $\beta\text{-Mg}_2\text{Al}_3$  and  $\gamma\text{-Mg}_{17}\text{Al}_{12}$  in order, is obtained on the AZ91D Mg surface [59,63].

- 2) Thermal treatment of Zn/Sn plated coating on an AZ91D alloy [64]

In this the heat treatment is carried out at about  $190 \pm 10$  °C for 12 h which results in the formation of a layer of  $\text{Mg}_2\text{Sn}$ , and this has better corrosion resistance when compared to the plated Zn–Sn coating in NaCl solution.

- 3) Metal cladding [65–67]

In this the metal sheets are bonded together under the simultaneous influence of the temperature and pressure to form a diffusion coating at the interface between the metal sheets. A localized melting takes place during the heat treatment as this process is generally performed at a high temperature (above 450 °C) and under a high pressure. The final microstructure present in the reaction zone can contain several second phases like  $\text{Mg}_{17}\text{Al}_{12}$  and  $\text{Mg}_2\text{Al}_3$  [65–67]. The good density obtained and the possibility of applying thicker coatings are some advantages of this technique.

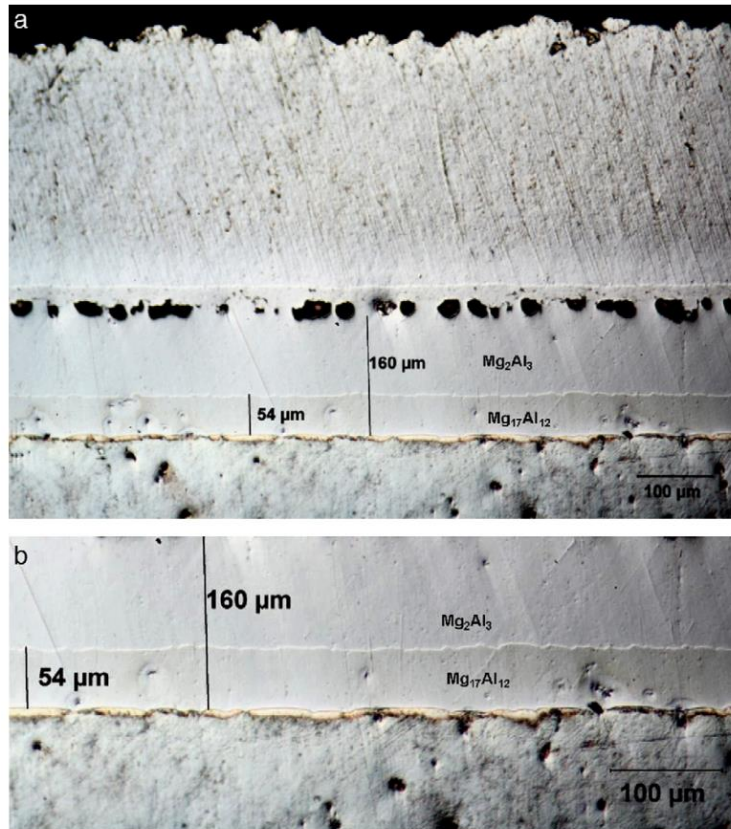


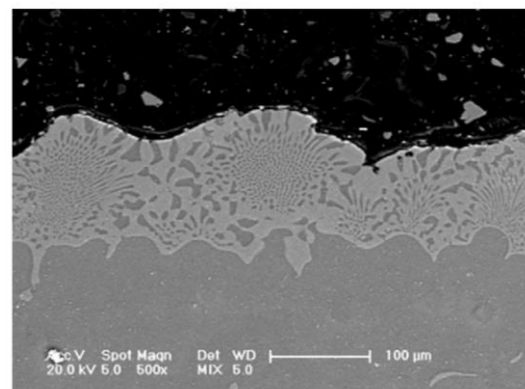
Fig. 1. (a) Typical optical micrographs showing both the  $Mg_2Al_3$  layer and the  $Mg_{17}Al_{12}$  phase layer before removing the un-reacted Al deposition (b) and after removing the Al deposition [68]

### 3. STRUCTURE OF THE DIFFUSION COATINGS

Every diffusion coating is characterized by the presence of an alloy-layer and the extent of alloying is dependent on the type of coating process. A part of the coating can be of an unalloyed coating metal. The phase composition and microstructure of the diffusion coating vary with system parameters such as coating methods, treatment time and temperature (this being the most dominating factor in the microstructure of the diffusion coating). As an example shown in Fig. 1 are the aluminium diffusion coatings formed at lower temperatures of around 200–400 °C tend to have layered continuous intermetallic compounds on the surface, irrespective of the treatment time and the coating technique [68]. Whereas, we always get the formation of a two-phase structure enriched in  $\gamma$ - $Mg_{17}Al_{12}$  (i.e.,  $\alpha$ -Mg +  $\gamma$ - $Mg_{17}Al_{12}$ ) on treatment at higher temperatures of around 420–470 °C as shown in Fig. 2 [59]. This also does not depend on the coating methods.

Fig. 2. Cross-section micrograph (backscatter SEM image) [59]

Two simple models for the evolution of the surface layer on Mg alloys during aluminizing, based on the coating temperature are shown in Fig. 3. Fig. 3(a) For aluminizing temperatures below the Mg–Al eutectic reaction (437 °C), first the active Al atoms are deposited on the substrate surface and then, these Al atoms which are absorbed at the surface diffuse into Mg to form  $Mg(Al)$  solid solution as shown in the top of Fig. 3(a). The concentration of Al on the top surface layer keeps rising as the diffusion process proceeds. This process continues until the  $\alpha$ -Mg matrix can no longer dissolve Al at the interface between the substrate and the Al medium., that is when the Al concentration in the top surface exceeds the solid solubility of Al in Mg at a certain temperature which can be seen from the Mg–Al phase diagram (Fig. 4) [69]. In the middle Fig. 3(a), we see a reaction occurring at the interface resulting in the formation of a new phase (i.e.,  $\gamma$ - $Mg_{17}Al_{12}$ ). At the surface,





there is an aluminium concentration jump. Similarly, as shown in the bottom Fig. 3(a), once more there takes place a phase transformation at the surface resulting in the generation of a second  $\beta$ - $\text{Mg}_2\text{Al}_3$  layer when the Al concentration at the surface becomes higher than the one acceptable in  $\text{Mg}_{17}\text{Al}_{12}$ . At coating temperatures higher than  $420^\circ\text{C}$ , the  $\text{Mg}/\text{Mg}_{17}\text{Al}_{12}$  eutectic reaction takes place ( $\text{L} \leftrightarrow \alpha\text{-Mg} + \gamma\text{-Mg}_{17}\text{Al}_{12}$ ) since this temperature is near or higher than the  $\text{Mg}$ – $\text{Al}$  melting point or eutectic reaction point ( $437^\circ\text{C}$ ). This is shown in Fig. 3(b) where a two-phase structure or discontinuous distribution of the  $\text{Mg}_{17}\text{Al}_{12}$  intermetallic phases is obtained.

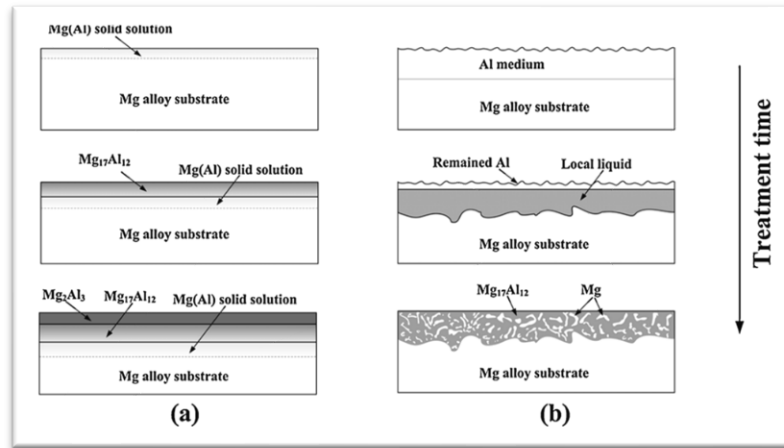


Fig. 3. Schematic diagram of the growth of the surface layers on Mg during the diffusion coating process. (a) is applicable for the lower temperature process (below  $437^\circ\text{C}$ ) and (b) is for the higher temperature process (near or above  $437^\circ\text{C}$ ) [1]

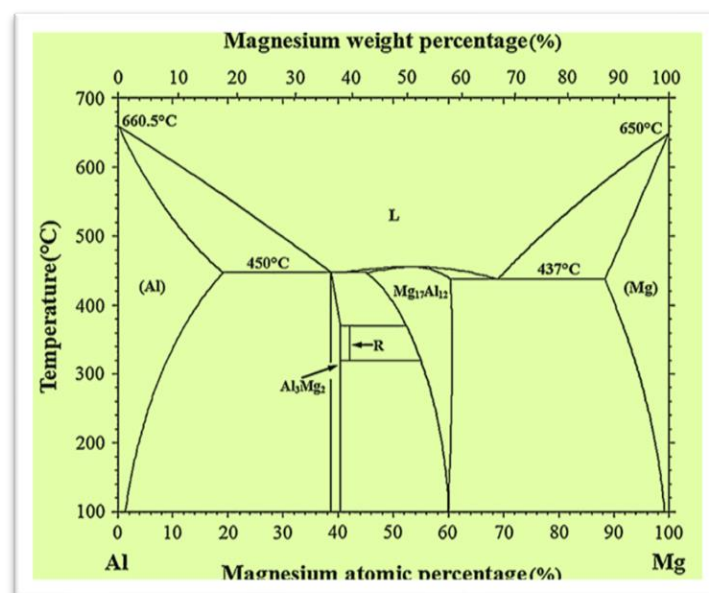


Fig. 4. Mg–Al binary phase diagrams [69]

#### 4. CONCLUSION

In this study we discussed and reviewed the recent findings of diffusion coatings on Mg and its alloys. It is evident that we can achieve a combination of high hardness and good resistance to corrosion and wear to Mg alloys by diffusion coatings, while preserving the unique properties of the Mg alloys such as the electrical and heat conductivities. In this study we reviewed several coating methods comprising both single and combined processes to fabricate diffusion coatings on magnesium and its alloys. We concluded that among several processing parameters, treatment temperature plays a main role in deciding the final microstructures and properties of the diffusion coatings.

As diffusion coating is a high temperature process, it may have negative effects on the Mg



alloy substrate. This is a major challenge associated with the diffusion coating. Therefore, we discussed some works aiming at lowering the coating treatment temperature of Mg and its alloys. This can be done by enhancing the activity and diffusivity of the atoms utilized for coating. Much research has taken place on simple Al diffusion coatings and complex multicomponent diffusion coatings will continue to be explored in the future as a path to increase further the surface properties of Mg alloys.

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