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Droplet spraying of aluminum on magnesium

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Abstract: An Al coating on Mg substrate was achieved by droplet spraying treatment. The microstructure was studied by electron probe microanalysis (EPMA) and X-ray diffraction (XRD). The coating layer is composed of Al phase and exhibits superior corrosion resistance. The formation of the coating is mainly attributed to the obstruction of expansion of the transition zone by primarily solidified $Mg_{17}Al_{12}$ during rapid cooling, and the diffusion is restricted in a thin layer. These results show that droplet spraying is a promising way to protect magnesium by using corrosion-resistant materials available now.

Key words: droplet spraying; coating; magnesium; corrosion resistance; rapid solidification

1 Introduction

Magnesium based alloys attract great interest in the automobile and electric industry due to their superior properties including high specific strength, good damping capability, excellent machinability, good electromagnetic shielding and recyclability. However, the poor surface properties of magnesium alloys limit their applications, especially in the aggressive environments. Therefore, attempts are made to improve wear and corrosion resistance of magnesium based alloys by surface treatment [1−3]. There are a number of possible surface modification technologies available for magnesium and its alloys, such as anodizing, conversion coating, electrochemical plating, electroless nickel plating, microarc oxidation, thermal spray coating, and laser surface treatment [2−4]. Among these coating methods, thermal/cold spray and laser surface treatment have attracted great interest of many researchers in recent years because these processing methods can provide thicker alloy coatings. The most widely used coating materials for protective coatings on Mg include Al and Al based alloys, due to their good compatibility with Mg.

Thermal spray and cold spray techniques have been shown potential for the surface modification of Mg alloys [5−6]. Al based alloys have been coated by thermal/cold spraying on Mg alloys to improve the surface corrosion resistance [7−8]. Nevertheless, the adhesion strength of thermal spray coatings on magnesium alloys is not sufficient, so the following post-treatment processes are always performed. One of such possibilities is laser remelting of thermally sprayed coatings, where the mechanical bond between the substrate and the coating may change to metallurgic bond after laser treatment [8]. Laser surface modification technique is an alternative technology of magnesium alloys. Laser surface re-melting [9], laser surface alloying, and laser cladding of magnesium alloys, as reported in a number of studies, can improve corrosion or wear resistance for pure Mg and Mg alloys which have been surface alloyed with Al [10], Al+Si [11], Al+Cu [12], even amorphous and ceramic composites [13−14]. For laser surface treatment, a metallic coating and the underlying substrate are melted using a high power laser. The rapid melting, mixing and resolidification lead to chemical composition change and formation of new phases in the melted layer [10−11]. Chemical composition of coatings will be out of control due to the excessive diffusion of magnesium into the laser-melted surface, so it is difficult to get desired coatings designed for special environments.

Recently, the uniform droplet spray (UDS) process has emerged as one efficient net forming technology of metal parts, in which molten metal droplets are ejected through the nozzle to the inert gas environment by applying static pressure on the bulk liquid material in the generator, and then dropwise deposit onto a movable substrate to fabricate three-dimensional prototypes [15]. Because of the precisely controlled temperature, trajectory and solidification of droplets, this technology

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is suitable for the coating of alloys on metal substrate.

In the previous work [16], Al phase coating on AZ91 substrate was obtained by droplet spraying method. The coating exhibits almost the same properties as those of the original coating material of as-cast Al.

In order to have a better understanding of the droplet spraying mechanisms, Al was deposited by droplet spraying process on pure Mg in this work. The influences of droplet spraying on microstructure and corrosion resistance were studied.

2 Experimental

The substrate Mg piece with the size of 10 mm×50 mm×50 mm was cut from commercial magnesium ingot with purity of 99.5% (mass fraction). The original coating material used in this work was cut from commercial Al ingot with purity of 99.7% (mass fraction). A droplet spraying system was developed, as shown schematically in Fig. 1. Metal droplet was produced by pushing molten metal through the nozzle under the pressure of argon. The droplet was then deposited on the substrate and a coating formed after solidification. Just before droplet spraying, the specimens were mechanically polished with 600-grit abrasive paper in order to produce a fresh surface free from oxides and contaminants.

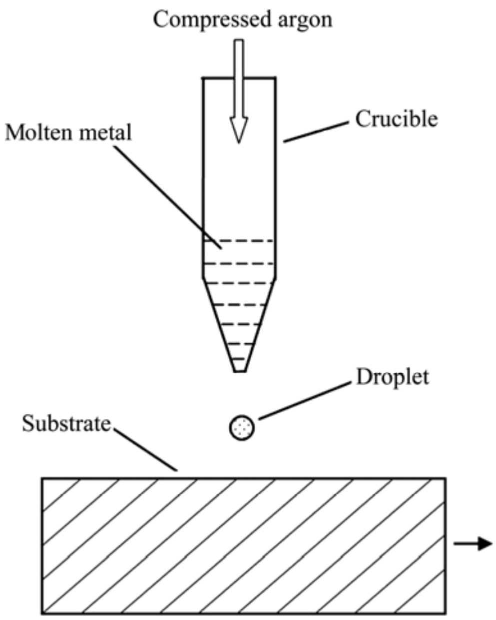

Fig. 1 Schematic diagram of droplet spraying process

The cross-sectional micrographs and the chemical compositions were obtained by using JXA-8230 electron probe microanalysis (EPMA), coupled with the Oxford INCA X-ray microanalysis system. The sample was etched with a solution of 3% (volume fraction) nitric acid alcohol. The phase compositions of the interfacial zone were studied by X-ray diffraction (XRD) with a Rigaku D/MAX-2500 diffractometer using Cu K_α radiation in a θ–2θ geometry. In order to get more phase information including interface, as well as coating and substrate, careful adjustment was performed to make sure that the X-ray scans along the central line of the interface. Electrochemical measurement was done with LK2005 Potentiostats-Electrochemistry Workstation in a 3.5% NaCl (volume fraction) solution, and a saturated calomel electrode was used as reference electrode.

3 Results and discussion

3.1 Microstructure and phase analysis

Figure 2 shows the morphology of a cross-section of the droplet spraying coating obtained on the Mg substrate, in which an interface can be seen between the coating and the substrate.

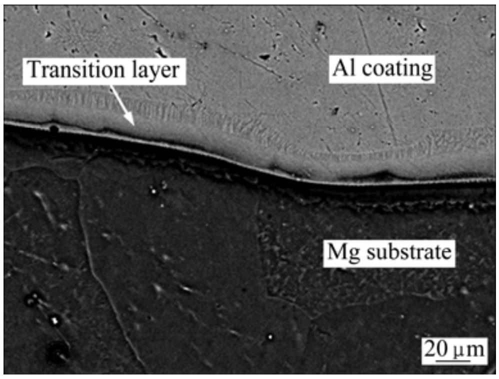

Fig. 2 Cross-section morphology of Al coating on Mg substrate obtained by droplet spraying

Figure 3 gives EDS elements line scanning in the vicinity of the interface. From Fig. 2 and Fig. 3, it is seen that there are three different zones, through the transition layer to the coating, with microstructure varied from the substrate. From the EDS profiling of Mg and Al in vertical direction on the interface (Fig. 3(a)), we can find that content of Al decreases while content of Mg increases gradually from substrate to the coating. And the contents of Mg and Al keep constant in the substrate and coating. It is clear that the interdiffusion between Mg and Al occurs during droplet spraying process.

The approximate contents of major alloying elements detected by EDS analysis on the cross section (points 1−5 in Fig. 3(b)), are presented in Table 1. The coating, substrate and transition zone are deduced to be Al solid solution, Mg solid solution and $Mg_{17}Al_{12}$, respectively, based on the Al-Mg phase diagram.

The XRD pattern on the cross section of the droplet spraying specimen is illustrated in Fig. 4. It can be seen that the main phases are Al and Mg, and very weak reflections of $Mg_{17}Al_{12}$ phase are also recognized. This is obviously different to laser surface treatment samples.

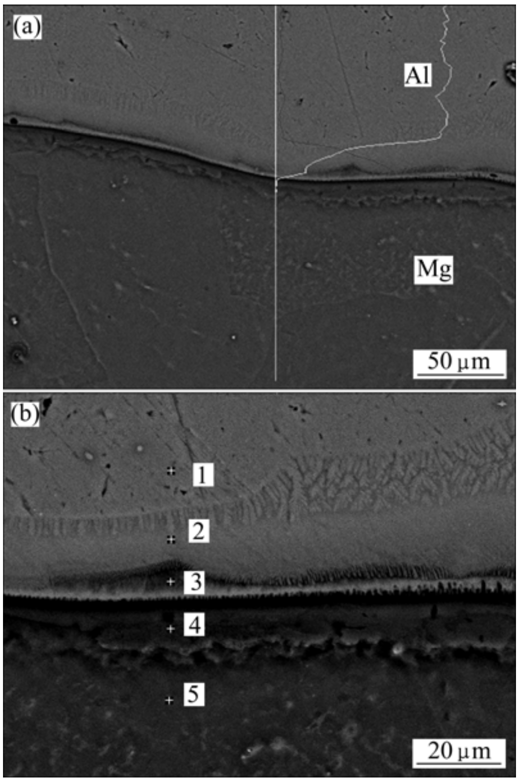

Fig. 3 Chemical composition changes from substrate to coating through transition layer

When Mg alloy is treated by laser cladding with Al, Mg-Al intermetallics are favored to form throughout the entire coating layer because of the violent mixing of the molten metal in the pool [10−12].

Table 1 Chemical composition of marked points in Fig. 3(b)

Point in Fig. 3(b)	x(Mg)%	x(Al)%
1	2.28	97.72
2	48.42	51.58
3	54.75	46.25
4	99.09	0.91
5	99.46	0.54

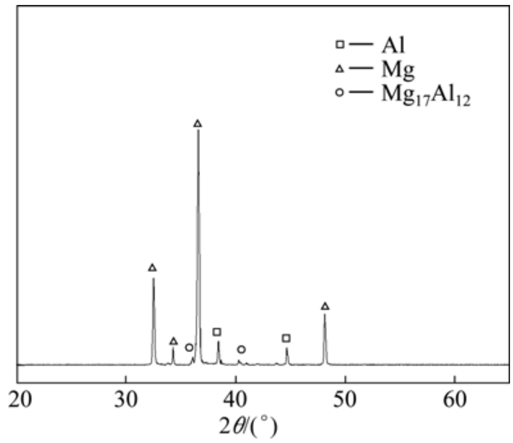

Fig. 4 XRD pattern of cross section

3.2 Formation mechanisms of Al coating obtained by droplet spraying

The formation mechanism of Al coating on Mg is schematically described in Fig. 5. The deposition process of a single droplet can be divided into four stages, as shown in Fig. 5(a). The content profiles and the temperature distribution curve in direction perpendicular

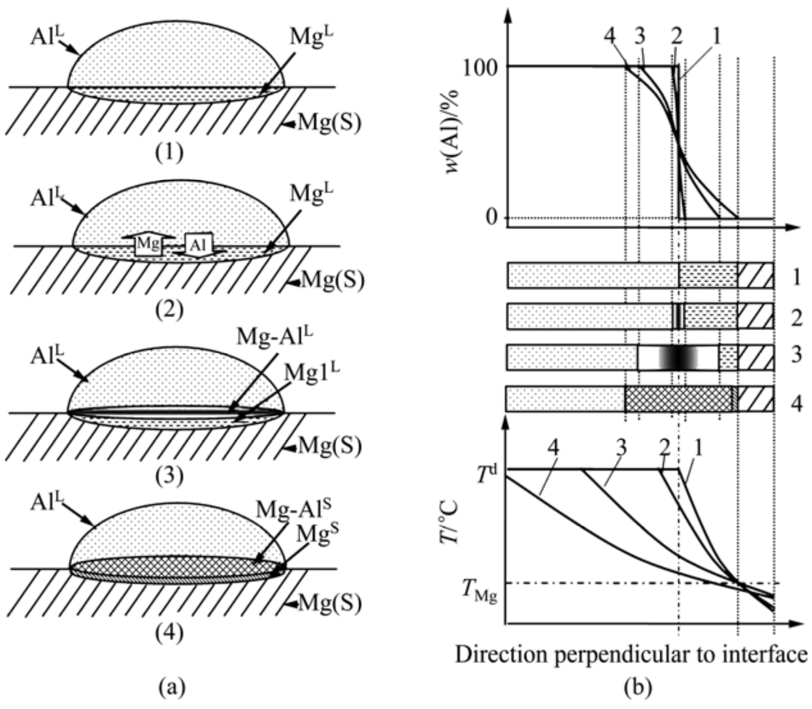

Fig. 5 Schematic diagrams of mechanism for droplet spraying: (a) Four stages of deposition process; (b) Composition distribution and temperature distribution in direction perpendicular to interface for different stages (T^d—Temperature of droplet; T_{Mg}—Melting temperature of Mg)

to the interface are schematically described in Fig. 5(b).

High temperature Al droplets (Al^L in Fig. 5(a)) deposit on the surface of Mg substrate (Mg(S) in Fig. 5(a)), and rapidly raise the Mg surface temperature as the heat is transmitted from Al^L to Mg(S), leading to the formation of a thin layer of remelting Mg (Mg^L in Fig. 5(a)(1)) when the surface temperature is higher than the melting temperature of Mg. As a result, two kinds of liquid metals contact with each other (Al^L and Mg^L), and elements diffusion occurs at the Al^L/Mg^L interface due to large content gradient between the two melts, that is, Al diffuses from the droplet (Al^L) into the re-melted Mg pool (Mg^L), while Mg diffuses to the opposite direction (Fig. 5(a)(2)). The diffusion leads to the chemical composition change of the melts and the formation of the transition zone ($Mg\text{-}Al^L$ in Fig. 5(a)(3)) between the two kinds of melts. The boundary of the transition zone consists of $Mg\text{-}Al^L/Mg^L$ interface and $Mg\text{-}Al^L/Al^L$ interface. As diffusion continues, migrating of the liquid−liquid interfaces and thickening of the transition zone take place.

It can be seen from Fig. 5(b) that the content profiles and the temperature distribution curve vary at different stages. The migrating of the interfaces is related to the position of the curves and will stop as the temperature at $Mg\text{-}Al^L/Mg^L$ interface drops below the melting temperature of $Mg\text{-}Al^L$, and this determines the final thickness of the transition zone. It should be noted that the droplet spraying is a kind of localized treatment, the conduction of the minimal heat into the relatively cool bulk leads to rapid quenching rates, and the solidification starts from the transition zone for it is closer to the cold substrate. As a result, further diffusion will be blocked by the frozen transition layer ($Mg\text{-}Al^S$ in Fig. 5(a)(4)), and element changes are restricted in a relatively thin transition zones, as shown in Fig. 5 and Fig. 3.

The transition zone enriched in Mg and Al atoms is near to $Mg_{17}Al_{12}$ phase region in Al-Mg binary phase diagram and favors to form $Mg_{17}Al_{12}$ phase during solidification, which is confirmed by XRD analysis. Due to high diffusion coefficients and low density, small amount of Mg is present in coating layer (as shown in Fig. 3(a) and Table 1). This Mg phase will solid-soluable in Al, and the final solidified coating is composed of Al phase.

3.3 Corrosion resistance

Potentiodynamic polarization curves for the coating and the substrate measured in a 3.5% (volume fraction) NaCl solution at room temperature are shown in Fig. 6, which represents the corrosion resistance of these specimens. The results show that the coating is superior to the substrate in corrosion properties. It can be seen from Fig. 6 that the corrosion potential of the coating is −1.43 V, which is 300 mV higher than that of the substrate, indicating that the coating is less active than the substrate. The corrosion current decreases by two orders of magnitude compared to that of the substrate. Furthermore, the substrate exhibits an activated-controlled anodic behavior while the coating shows an obvious passive behaviour. This indicates that the corrosion resistance of the coating is much higher than that of the substrate, which agrees with the chemical composition of the samples.

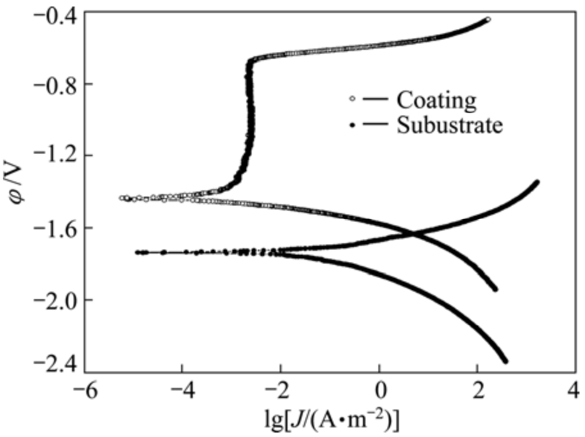

Fig. 6 Comparison of potentiodynamic curves for surface of coating and substrate

It is well known that both Al and Mg have low electrochemical potential. But the oxide film formed on Mg surface is very loose and porous, and it cannot offer effective resistance to corrosion; while the oxide layer on Al surface is dense enough to provide good protection to substrate [5]. So, the Al coating on Mg prepared by droplet spraying shows the same corrosion behavior as as-cast Al.

4 Conclusions

1) It is possible to produce an Al coating on the surface of Mg by droplet spraying process. The coating is metallurgically bonded with the substrate.

2) The coating is composed of Al phase. The formation mechanism of the coating is related to the droplet spraying process, in which the diffusion is restricted in a relatively thin transition zone due to the obstruction of diffusion by primary solidified $Mg_{17}Al_{12}$.

3) The corrosion resistance of Al coating in 3.5% NaCl solution is considerably higher than that of the Mg substrate, due to the chemical and phase composition of the coating.

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