Study on Effects of Heat Treatment on Morphology of Al Coating on the Surface of Mg Alloy by Cold Spray

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Abstract. The special pure aluminum coating was prepared on the surface of the as-cast AZ80 magnesium alloy by using the advanced technique named cold gas dynamic spray (CGDS). The interface morphology of coatings and substrate were observed. With the changes of the heat treatment temperature and the holding time, the interface morphologies of the coatings and the magnesium substrate were compared and the diffusion phenomena of them were studied. The experimental results showed that the great changes had taken place in the interface morphology of the coatings. Meanwhile, the great changes had also taken place in the diffusion between the magnesium in the substrate and the aluminum in the coatings. However, the diffusions between them were not obvious any more when the heat treatment temperature reached a definite value.

Introduction

Currently, magnesium alloy whose density is 1.75～1.90g/cm^3 is the lightest structural metallic material in practice. Although the strength and elastic modulus of magnesium alloy are lower, its specific strength and specific stiffness are higher. The usage of magnesium alloy makes component achieve higher stiffness and better weight-loss effect than the usage of aluminum in the component with same weight. Besides, magnesium alloy has such advantages as abundant natural resources and green environmental protection. It is the key structural material to realize the light productions of the military and civilian equipments, which has been received the close attention of all over the world [1-3]. In recent years, the applications has grown rapidly in the field of industry such as automobile, machine building, shipbuilding, agricultural machinery, aerospace, weaponry and equipment, electric engineering, instrument industries. Magnesium alloy achieves the purpose of not only the weight-loss but also the reduction of pollutant emissions, which directly affects the social and economic efficiency. Therefore, magnesium alloy are represented as the green engineering material with great potential and future in the 21st century.

Although magnesium alloy has many merit mentioned above, it has also such defects as softer, lower intensity and wear-resisting. Besides, it is the alloy with active chemical property. Therefore, it is easier for magnesium alloy to generate the corrosion phenomenon at the environment of the humid atmosphere, moisture and the acid-base liquor. And it is easier to oxidize rapidly with air and to create the galvanic corrosion with the metal or alloy with the greater electrode potential. Furthermore, magnesium alloy is loose and porous, which is not as compacted as aluminum with oxidation film. Thus, the corrosion property of the magnesium and magnesium alloy is very poor. All of them mentioned above affect the applications of magnesium alloy in military and civil industry. The wear and corrosion of the magnesium alloy has been becoming one of the key technologies in the application. Therefore, the study on the surface engineering about the corrosion resistant technique of magnesium alloy should be performed immediately.

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Currently, the common methods on surface protecting of magnesium alloy have anodic oxidation treatment, micro-arc oxidation treatment, vapor deposition process, ion implantation, electroplating, laser surface modification, chemical conversion film treatment, etc. Most of the methods have many defects such as poor process repeatability, high price, microporous in the film, cracks. Especially, they have toxicity, pollutions on the environment and high cost of waste liquid treatment [4-9]. In recent years, the traditional thermal spray technologies of magnesium alloy protecting have been reported. However, the higher temperature in the process of thermal spray may generate such problems as high temperature oxidation, crystallization, residual stress, cracks and desquamation, etc. Therefore, to find a kind of the surface coatings technique with the environment protection and economic feasibility on magnesium alloy is the problem to be settled.

Against this background, the application of cold gas dynamic spray (CGDS) technology on the preparation of corrosion resistant coatings is born at the right moment. Thus, not only can the all abuse of the technologies mentioned above be avoided, but the effective protection on the lightweight materials like magnesium alloy can be performed. Besides, the CGDS technology has two remarkable features: one is lower temperature (＜600°C) and the other is higher velocity (300～1200m/s), which has ability to avoid the oxidation of the coatings. Therefore, the coatings with low oxidations, low stress and heavy thickness can be obtained. However, the bonding style between the substrate and the coating obtained by CGDS is the mechanical bond. Therefore, the bonding strength of them is relatively low. In this study, the method of the annealing treatment was employed to achieve the interdiffusion between Mg and Al existing in the substrate and coating, respectively. In this case, the metallurgical bonding could be obtained. Ultimately, the bond strength could be improved. On this basis, the optimum heat treatment technique was established.

Experiment

Experiment material

The substrate is magnesium alloy AZ80. Its chemical composition is shown in Table1. The material of coating is the imported Al powder which is exclusive for CGDS technology. Its grit size is 300 meshes.

Table 1. Chemical composition of the substrate (wt.%)

Al	Zn	Mn	Fe	Ni	Si	Cu
8.05	0.480	0.220	＜0.005	＜0.001	＜0.01	＜0.005

Nitrogen is chosen as the process gas and carrier gas in this study. The reason is that the price of nitrogen is low and the process technology of the coating also is considered. Meanwhile, according to the theory of the molecular kinetic, the carrier capacity of gas is relative to the ratio of specific heat γ. The higher the value of γ is, the higher the capacity of carrier. And γ is relative to the molecular freedom of gas n. The correlation between the two is shown as below,

$$\gamma = \frac{n+2}{n} = 1 + \frac{2}{n}. \tag{1}$$

It follows from the Eq. 1that the smaller the value of n, the higher the γ. That is to say, the capacity of carrier is high. To the diatomic gas like nitrogen, $n = 5$, $\gamma = 1.4$. However, according to Eq. 1, the γ value of helium gas is 1.67. Obviously, this value is higher than that of nitrogen. However, the cost of helium is far higher than that of nitrogen. Therefore, taking all of these factors together, nitrogen was chosen as the process gas in this study.

Experiment method

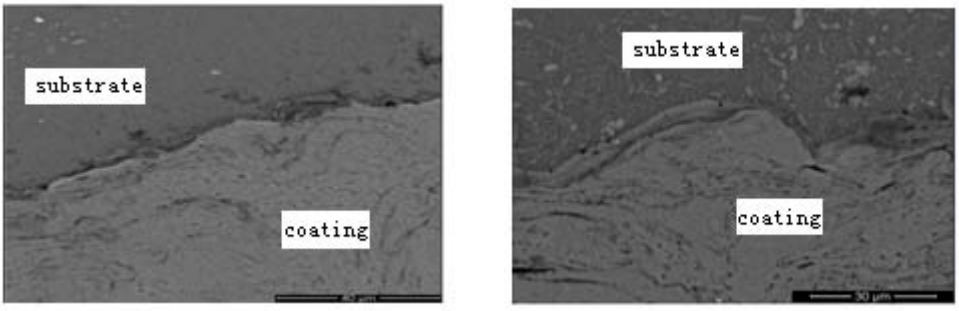
Because it is easy for magnesium alloy to oxidize, the oxidation speed is also fast even in the air. Therefore, before the experiment was performed, the substrate should be washed by acetone firstly, and then the grit blasting was taken. Then, the experiment was done immediately. The substantial work was that the substrates with coatings were put into for annealing heat treatment in 200°C, 250°C and 300°C, respectively. The holding time was 1h, 2hs and 3hs, respectively. The interface between

the substrate and coating was scanned by SEM, and their morphologies were observed. The interdiffusion of magnesium in the substrate and aluminum in the coating was analyzed by EDS at the conditions of different annealing temperature.

Experimental results and analysis

Effects of annealing treatment on the morphology of coatings

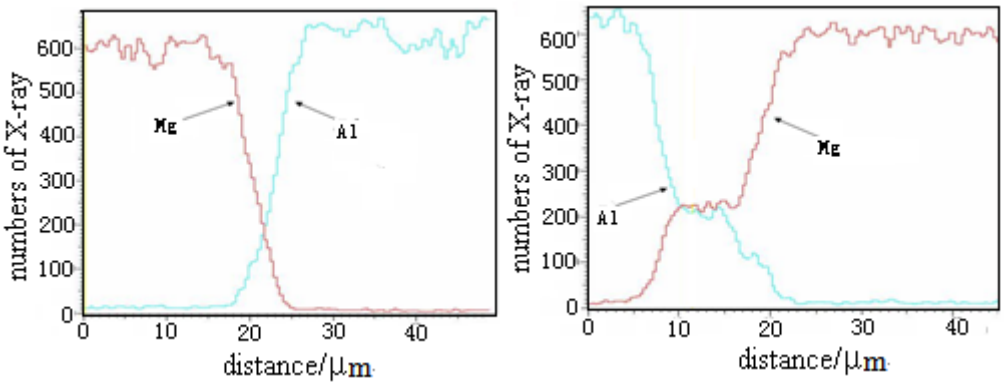
It is upon the formation principle of cold spray that the intense plastic deformation happens in the interface of the particle and the substrate, and the shape of the particles with globular shape and spheroidic particles become flat and strip. The bonding principle is physical bonding and mechanical bonding. All is well known the bond strength of the coating obtained by the physical bonding and mechanical bond is low relatively, which results in the abscission of coating. As a result, the heat treatment is widely used in order to obtain the higher adhesion between the substrate and coating. To illustrate the effects of annealing treatment on the coating morphology, the comparisons of the coating morphology without the annealing treatment and that with the annealing treatment were executed.



(a) Without heat treatment, air-cooled (b) 250°C, holding time1h, air-cooled

Fig.1. Interface morphology of coating and substrate

As is shown in Fig.1 (a), no heat treatments were made and air-cooled was executed after spraying. It is also seen from this figure that the interface of coating and the substrate is clear, regular and coherent. Most importantly, no defects occur. As a result, the key bond mode of the coating and the substrate is mechanical bond. The interface morphology of coating and the substrate was obtained at the temperature of 250°C for one hour. It is seen from the fig.1 (b) that the interface of coating and the substrate is accidental, which indicates that the bond mode is metallurgical bonding. It is also seen from the changeable curve of the number of X ray about the Mg and Al shown in fig.2 that, after the annealing treatment, the diffusion phenomena between the coating and the substrate occur. The coating is shown in the left partial of the fig.2 (a) and the substrate in right partial. The coating was taken without heat treatment. It can be seen from this figure that the contents of Al is decreasing but that of Mg is rising. However, the contents of Al and Mg have no changes near the interface, which indicates that there is no diffusion in this position. Compared with the fig.2 (a), the contents of the fig.2 (b) are different obviously. Although the contents of Mg from the substrate to the coating are decreasing and that of Al is rising, they have been greatly changed near the interface. These perfectly illustrate that the diffusions between the Mg and Al occur with annealing treatment. However, the diffusion phenomena of other elements didn’t occur in the substrate.



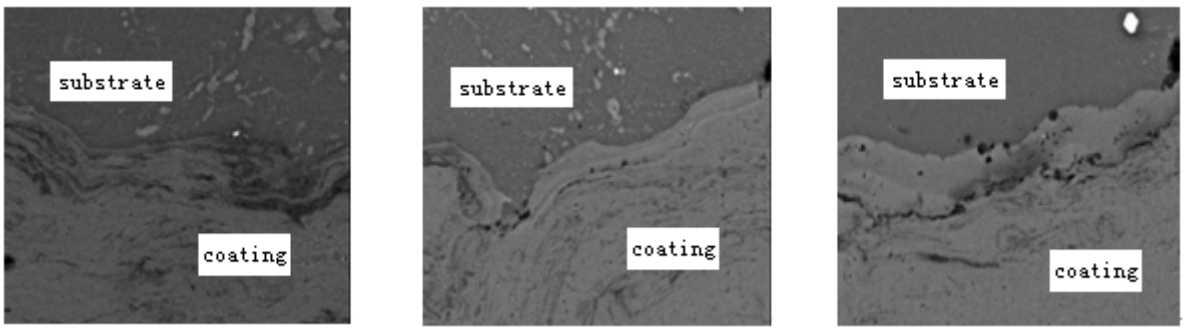
(a) Without heat treatment, air-cooled (b) 250°C, holding time1h, air-cooled

Fig.2. Diffusion of Mg and Al

The reason for the diffusion phenomena of Mg and Al in annealing treatment is relative with the lattice style. The structure of Magnesium alloy is the close-packed hexagonal structure and that of Al is the face-centered cubic structure. Generally speaking, the activation energy of the diffusing atom in the close-packed hexagonal structure is bigger than that in not close-packed hexagonal structure, which generates the results that the diffusion coefficients of the diffusing atom in different crystal structure are different greatly[10]. The diffusion of Al in Magnesium alloy needs more activation energy than that of Mg in the coating. The plastic yield of alloy powder in the coating in the process of CGDS is high, and the high-density dislocation is formed. As a result, the surface activation energy rises, which contribute immensely to the diffusion of Mg to the coating. Generally, the atoms near the intergranular are looser, and their energies are high. Therefore, they have lower diffusion activation energy and higher diffusion velocity. The coating consists of massive fine particles which generates many intergranular. These intergranular become the diffusion entryway of the atoms in the substrate to coating. The reasons above lead to the results that the diffusions from Mg to the coating are stronger than that from Al to the substrate and the diffusion distances are farther. These diffusions contribute immensely to the homogenization of the coating tissue, which may reinforce the coating. Meanwhile, the diffusions are beneficial to the transition of the coating from mechanical bonding to metallurgical bonding and to the improvement of the bonding strength of the interface.

Effects of the different annealing temperature on the morphology of coatings

To illustrate the effects of the different annealing temperature on the morphology coatings, the 200°C, 250°C and 300°C were taken as the annealing temperature, and the holding time was identical. As is shown in fig.3, the morphology coatings in 200°C, 250°C and 300°C are shown in fig3(a), fig3(b) and fig3(c), respectively. The transition layer occurs in the interface in 200°C, but the border is unsharp. By contrast, the obvious diffusion occurs in the interface in 250°C, and the border is sharp. As to 300°C, the transition layer is evened out and thick obviously.



(a) Without heat treatment, air-cooled (b) 250°C, holding time1h, air-cooled (c) 300°C, holding time1h, air-cooled

Fig.3. Interface morphology of coating and substrate in different annealing temperature

Because the segregation occurs between the grains and grain boundary, there is a kind of homogenization in the process of heat treatment. That is to say, the diffusion may happen between transgranular and the grain boundary. With the improvement of the heat treatment temperature and

the extension of time, the interfaces among grains in the coating may disappear. At last, a homogeneous integrality is obtained. In this process, the diffusions between the substrate and the coating happen. However, with the disappearance of the interface in the coating, the diffusion aisle decreases, which makes the diffusion velocity decrease. Ultimately, the effects of the heat treatment temperature and time on the diffusion decrease. The experimental results in this study may illustrate these cases. Besides, because the substrate is magnesium alloy which might easily produce overheat and oxidation, the heat treatment temperature should not be too high and the time should not be too long.

Conclusions

With the methods of heat treatment, the diffusion of Mg and Al took place between the Al coating sprayed on the surface of the Magnesium alloy and this substrate, and the diffusion degree was high. However, their diffusion degrees were different. The diffusion degree of Mg to the coating was higher than that of Al to the substrate.

With the increase of the heat treatment temperature, the diffusions were increased in different degree. When the annealing temperature was 200°C, the transition layer occurred in the interface, but the border is unsharp. When the annealing temperature was 250°C, the obvious diffusion occurred in the interface, and the border is sharp. As to 300°C, the transition layer is evened out and thick obviously.

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