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The Role of Ammonium Chloride in the Powder Thermal Diffusion Alloying Process on a Magnesium Alloy

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Abstract: The powder thermal diffusion alloying method could be utilized to fabricate Al-rich intermetallic coatings on magnesium alloys in the air. While the role of ammonium chloride powder in the diffusion alloying source is still to be investigated. This research took the AZ91D magnesium alloy as the substrate. Diffusion sources with various powders were utilized as the diffusion source. Microstructure observation and phase identification were enrolled to investigate the role of the ammonium chloride powder in the diffusion alloying process. Results indicate that HCl gas could turn some solid Al powder into gaseous AlCl_3 to enhance the transport of active Al atoms, moreover, it reacts with the dense MgO film and converts it to a loose one, which enables the AlCl_3 gas to penetrate MgO and arrive the matrix to form a protective coating. Furthermore, the ammonium chloride content should be confined to 10 wt. % of the diffusion alloying source. Too much ammonium chloride powder would result in a worse intermetallic coating.

Keywords: magnesium alloy; ammonium chloride; diffusion; coating; powder

1. Introduction

Magnesium alloys are easy to be corroded and this limits their utilization [1–4]. To protect magnesium alloys from serious corrosion, various methods are raised. For example, magnesium alloys could be covered with coatings which are much more corrosion resistant [5–7].

By the diffusion alloying method, metallic atoms could be added to the matrix of magnesium alloys continuously for the corrosion resistant coatings to form [8–14]. Most of these diffusion alloyed coatings are obtained in a vacuum or inert atmosphere. While utilizing ammonium chloride as an activator, such a diffusion alloying process could be carried out even in the air [15,16].

The as-diffusion alloyed Al-rich intermetallic coating usually composed of two phases, a light phase and a dark phase [3,4,14–16]. The light phase has a network shape, and the dark phase is co-mingled in the light phase. The Al content of the light phase is much higher than that of the dark phase. The light phase is mainly composed of $\text{Mg}_{17}\text{Al}_{12}$, while the dark phase is mainly $\alpha\text{-Mg}$.

The Al-rich intermetallic layer integrates with the magnesium alloy matrix by metallurgical bonding, and such bonding could improve the adhesion strength greatly [4]. Compared with an ordinary specimen, the diffusion alloyed magnesium alloy specimen has better corrosion resistance

due to the formation of the Al-rich intermetallic layer [4,8,9,11,12]. The hardness of the Al-rich intermetallic layer is also higher than that of the magnesium alloy substrate [4,8,14].

It is commonly assumed that solid diffusion dominates the overall diffusion alloying process. While, after addition of some NH_4Cl powder as the activator, the mass transport process could be different from the traditional diffusion alloying process without the activator. Thus, it is meaningful to investigate mass transport in a powder thermal diffusion alloying process in the air.

Meanwhile, as the ammonium chloride powder could promote the formation of the intermetallic layer on magnesium alloys, how to utilize the ammonium chloride powder effectively is still an issue to be discussed. Generally, if the relative content of ammonium chloride powder in the mixed powder increases continuously, three circumstances could be encountered [17–20]. First, the increased ammonium chloride content would promote the formation of the intermetallic coating further. Second, the increased ammonium chloride content would have little effect on the intermetallic coatings. Third, the increased ammonium chloride content would have a negative effect on the intermetallic coating, in other words, both the thickness and completeness of the intermetallic coatings would be worse.

In this research, different diffusion alloying systems were designed and tested to clarify the role of ammonium chloride in the diffusion alloying process on the AZ91D magnesium alloy specimens. Furthermore, to utilize NH_4Cl powder effectively, powder thermal diffusion alloying processes with various NH_4Cl contents in the diffusion source were carried out to fabricate Al-rich intermetallic coatings on the AZ91D magnesium alloy specimens. It is hoped that the corresponding results would be helpful for utilizing NH_4Cl powder more rationally to fabricate better intermetallic coatings, to save materials and to alleviate air pollution and device degradation.

2. Experimental Details

An as-cast AZ91D magnesium alloy with the chemical composition shown in Table 1 was utilized as the substrate for packed powder diffusion alloying treatment. Samples with a dimension of 15 mm × 10 mm × 3 mm were cut from the magnesium alloy sheets with an electrical discharge cutting machine (Posittec, Suzhou, China) for experiments. These specimens were polished with SiC papers to 1000 grit, rinsed with alcohol, and then dried up.

Table 1. The chemical composition of the AZ91D magnesium alloy substrate.

Element (wt. %)	Al	Zn	Mn	Si	Fe	Cu	Ni	Mg
AZ91D	9.1	0.52	0.26	0.03	0.001	0.014	0.001	Balance

As the diffusion source, the mixed powder was composed of Al powder, Al_2O_3 powder and NH_4Cl powder. The size of the as utilized pure Al powder varies from tens of micrometers to hundreds of micrometers as shown in Figure 1a. The as utilized Al_2O_3 powder has a spherical morphology, the diameter of which varies from 100 to 300 μm as shown in Figure 1b. The as utilized NH_4Cl powder has a cubic morphology and a size which could even approach 1000 μm as shown in Figure 1c. Without specification, there would always be 10 g of Al powder, 10 g Al_2O_3 powder in the diffusion source. In this research, to investigate the effect of the NH_4Cl powder, the weight of NH_4Cl powder in the diffusion source varies. In different schemes, the contents of NH_4Cl powder were set to be 1, 2, 3, 4, and 5 g individually. Then the Al powder, the Al_2O_3 powder and the NH_4Cl powder were mixed together.

The mixed powder was put into a 30 mL ceramic crucible and the AZ91D magnesium alloy specimens were buried in the mixed powder. After the temperature in an ordinary resistance furnace reached 430 °C and was kept stable for a certain period, the fulfilled crucible was put into the furnace as quickly as possible and kept at 430 °C for 2 h for the diffusion alloying process to proceed. The whole diffusion alloying process was carried out in the air, neither vacuum nor inert gas was utilized.

When the diffusion alloying process finished, the specimens were taken out from the furnace and cooled down in the air.

Figure 1. The as-utilized powder (a) the pure Al powder, (b) the Al_2O_3 powder, (c) the NH_4Cl powder.

After the residual mixed powder was shaken off, the as-diffusion alloyed specimens were washed in running water and alcohol successively, and then dried up. Cross sections of specimens were obtained with a saw and then polished and etched for microstructure observation. Two etchants were utilized. One of which composed of 4 mL of nitric acid and 96 mL of alcohol. The other etchant composed of 6 g picric acid, 10 mL of glacial acetic acid, 10 mL of distilled water, and 70 mL of alcohol. The polished cross-sections of the specimens were etched until the intermetallic phases showed up clearly on the specimen surface. Then, specimens were washed with alcohol and dried up. Morphology of the cross sections of the as-diffusion alloyed specimens was observed by a tabletop microscope (TM3030, Hitachi, Tokyo, Japan) and a scanning electronic microscope (SEM, S-3400N, Hitachi, Tokyo, Japan). The phase identification was carried out utilizing an X-ray diffractometer (Ultima IV, Rigaku, Tokyo, Japan). The Gibbs energies were calculated by a software HSC 6.0.

3. Results and Discussion

3.1. Formation of the Intermetallic Coating on the AZ91D Magnesium Alloy

A coating was obtained by the compact powder diffusion alloying process with a diffusion source containing 1 g of NH_4Cl , 10 g of Al powder, 10 g of Al_2O_3 powder, and a cross-section of the as-diffusion alloyed specimen with the coating is shown in Figure 2a. It could be figured out that the thickness of the coating varies from tens of micrometers to one hundred micrometers. Moreover, as shown in Figure 3, the Mg element and the Al element coexist in the as-diffusion alloyed coating, which indicates that this coating is an intermetallic coating. Meanwhile, the Al content in the network-shape phase is obviously higher than that in the matrix, which indicates that the intermetallic coating is rich in Al. Additionally, there is mainly the $\text{Mg}_{17}\text{Al}_{12}$ phase and magnesium solid solution in the intermetallic layer [15].

The formation process of the as-diffusion alloyed intermetallic layer could be described as follows. At the beginning of the diffusion alloying process, the magnesium alloy specimen and the mixed powder contacted directly as shown in Figure 2b. As the diffusion alloying process went on, the NH_4Cl powder in the diffusion source decomposed into NH_3 gas and HCl gas, and the HCl gas reacted with the diffusion source to produce gaseous AlCl_3 . Meanwhile, on the surface of the magnesium alloy specimen, a loose MgO film formed. The AlCl_3 gas went through the loose MgO film to arrive at the magnesium alloys substrate. Thus, Al atoms were added continuously into the magnesium alloy's matrix. After the relative Al content on the magnesium alloy surface reached a limit, the local melt emerged according to the phase diagram [16] as shown in Figure 2c. After the diffusion alloying process, the Al-rich melt cooled down gradually, the magnesium solid solution phase and the $\text{Mg}_{17}\text{Al}_{12}$ phase solidified one after another [21]. Thus, a eutectic Al-rich coating is formed on the magnesium alloy specimen surface as shown in Figure 2d.

Figure 2. The microphotograph of the as-fabricated coating (a) and schematic diagrams to illustrate the formation process of the coating (b–d).

Figure 3. The cross-section of partial as-diffusion alloyed coating (a) and relative element distribution (b) on the line shown in (a). The arrow in (a) indicates an external Al-rich particle.

3.2. Ammonium Chloride Could Keep the Surface of the Magnesium Alloy Matrix Fresh

It is reported that [22] at the beginning of the oxidation process of magnesium alloys, a compact layer would emerge at the magnesium alloy surface, and such a dense layer could separate the diffusion source from the magnesium alloy matrix, thus the diffusion of active metal atoms and the growth of the intermetallic layer on magnesium alloy surface is interfered by a dense film as illustrated in Figure 4.

Chemical reactions involved in the powder thermal diffusion alloying process of our work are shown below. The Gibbs energies of these chemical reactions are shown in Figure 5.

Figure 4. The traditional powder thermal diffusion alloying process on magnesium alloys in a vacuum or inert atmosphere (a) and in the air (b).

Figure 5. The Gibbs energies of some chemical reactions in a thermal diffusion alloying process.

As the HCl gas which decomposed from the ammonium chloride powder could turn the pure Al powder into AlCl_3 gas as described in Equation (2), the diffusion source could then be changed from a mixture of Al, Al_2O_3 and NH_4Cl into a mixture of AlCl_3 and NH_4Cl . Hence, a diffusion alloying process with 1 g of AlCl_3 and 1 g of NH_4Cl as the diffusion source was carried out to testify whether such a new mixture could make an Al-rich intermetallic layer form. Meanwhile, in this experiment, a layer of SiO_2 powder separated the AZ91D magnesium alloy matrix from the diffusion source which was composed of AlCl_3 and NH_4Cl to investigate whether the AlCl_3 gas could pass through the SiO_2 barrier and arrive at the magnesium alloy matrix to form a coating. Schematic diagram of the diffusion alloying system is shown in Figure 6a.

Figure 6. (a) The illustration of the diffusion alloying system to prove the existence of vapor transport; (b) The as-diffusion alloyed intermetallic layer utilizing the diffusion alloying system shown in (a); (c) The source and movement of the AlCl_3 gas which carrying active Al atoms.

After the diffusion alloying process, an intermetallic coating formed on the magnesium alloy specimen as shown in Figure 6b. The thickness of the coating is near 100 μm . The mechanism could be explained as shown in Figure 6c. When heated up, the solid AlCl_3 powder became AlCl_3 gas. The AlCl_3 gas could penetrate the SiO_2 layer and the MgO film, and arrive at the magnesium alloy matrix to form an intermetallic coating.

An experiment was carried out to clarify whether it is possible to simplify the diffusion source which was composed of AlCl_3 and NH_4Cl further to a new diffusion source which was only composed the AlCl_3 powder. As shown in Figure 7a, there was only the AlCl_3 powder in the diffusion source. A layer of SiO_2 was also utilized to separate the magnesium alloy matrix from the diffusion source. After the diffusion alloying process, it is hard to find an intermetallic layer on the magnesium alloy specimen as shown in Figure 7b. This result illustrates that the NH_4Cl powder is important in a powder thermal diffusion alloying process on a magnesium alloy matrix. As shown in Figure 7c, if the diffusion source is lacking NH_4Cl , a compact MgO film could form on the surface of the magnesium alloy specimen. Thanks to the decomposition of the NH_4Cl powder, the HCl gas could turn a compact MgO film into a loose one as described in Equation (3) and (4), thus the AlCl_3 gas has the chance to penetrate the loose MgO film to arrive at the magnesium alloy matrix.

Figure 7. (a) The illustration of the powder thermal diffusion alloying system to investigate the effect of NH_4Cl on the MgO film; (b) Cross section of the as-diffusion alloyed specimen utilizing the diffusion system shown in (a); (c) Effect of the HCl gas on the MgO film.

3.3. The Upper Content Limit of the Ammonium Chloride in a Diffusion Alloying Process

Figure 8 shows the XRD patterns of the as-diffusion alloyed specimens with various diffusion sources containing 10 g Al powder, 10 g Al_2O_3 powder together with 1, 2, 3, 4, 5 g of NH_4Cl powder respectively. Peaks related to the Mg solid solution, MgO , and $\text{Mg}_{17}\text{Al}_{12}$ could be identified. The existence of the Mg solid solution and $\text{Mg}_{17}\text{Al}_{12}$ is consistent with the result shown in Figure 2a. Additionally, the existence of MgO is attributed to the preferential oxidation of Mg atoms [22,23]. It could be figured out that as the NH_4Cl content increases from 1 to 3 g gradually, the peaks of the $\text{Mg}_{17}\text{Al}_{12}$ phase in the XRD pattern became smaller and smaller, which means a continuously reduced quantity of the intermetallic layer. When the NH_4Cl content in the diffusion source passes over 3 g, the peaks of the $\text{Mg}_{17}\text{Al}_{12}$ phase could hardly be figured out, which means the quantity of the intermetallic phase on the magnesium specimens is limited. Thus, under the condition that there is 10 g of Al powder and 10 g of Al_2O_3 powder in the diffusion source, the content of the NH_4Cl powder is suggested to be no more than 2 g according to the XRD patterns shown in Figure 8. More generally, the weight of the NH_4Cl powder is suggested to be no more than 10% of the overall weight of the diffusion source.

As shown in Figure 9, after the powder thermal diffusion alloying process with a diffusion source which was composed of 5 g of NH_4Cl powder, 10 g of Al powder and 10 g of Al_2O_3 powder, both the

domain and the thickness of the intermetallic layer shrank obviously compared to that which was shown in Figure 2a. It is rare to find an intermetallic zone on the AZ91D magnesium alloy specimen surface. Figure 9a shows that there are even some local intermetallic zones occasionally, though their sizes are limited. The size of the local intermetallic zone as shown in Figure 9a is about 100 μm in length and the maximum thickness is around 30 μm . Both the size and the thickness of the intermetallic zone are unparalleled to that which is fabricated with the diffusion source, which contains 1 g of NH_4Cl . Figure 9b shows that it is rare to find an intermetallic zone at the specimen surface.

Figure 8. The x-ray diffraction (XRD) patterns of specimens which underwent various diffusion alloying processes with an NH_4Cl content of 1, 2, 3, 4, 5 g, respectively in the diffusion source. The triangles, pentagons, and quadrangles mark characteristic peaks of MgO , $\text{Mg}_{17}\text{Al}_{12}$ and Mg respectively.

Figure 9. The cross sections of the as-diffusion alloyed intermetallic layer fabricated with the diffusion source containing 5 g of NH_4Cl powder, 10 g of Al powder and 10 g of Al_2O_3 powder. Few intermetallic zones with limited sizes (a) could be found on the cross sections and most of the specimen surface is without any coating (b).

To investigate the effect of excess NH_4Cl powder further, a contrast test was conducted. Initially, an as-diffusion alloyed specimen was obtained by a powder thermal diffusion alloying process with 1 g of NH_4Cl powder, 10 g of Al powder and 10 g of Al_2O_3 powder as the diffusion source at 430 $^{\circ}\text{C}$ for 2 h. Then, the as-diffusion alloyed specimen was cut into two pieces, one of which was observed by a scanning electron microscope directly and the other piece underwent another heating process which was carried out at 430 $^{\circ}\text{C}$ for 2 h, the diffusion source of which contained 20 g of SiO_2 powder and 3 g of NH_4Cl powder. No Al powder or Al_2O_3 powder was involved in the second diffusion source.

Since no Al atoms were added into the intermetallic layer, the effect of the excess NH_4Cl powder on the as-formed intermetallic layer would be much more pronounced.

As shown in Figure 10a, the thickness of the intermetallic layer on the original specimen was around 100 μm and the intermetallic layer was continuous and relatively complete. While, as shown in Figure 10b, after another heat treatment with excess NH_4Cl powder, only a few local intermetallic zones are found on the magnesium alloy specimen surface, the thickness of the local intermetallic zone is no more than 50 μm . Moreover, the as-eroded specimen has a much more curved surface. This confirms that the excess NH_4Cl powder could deteriorate the newly formed intermetallic layer, hence, both the thickness and the domain of the intermetallic layer was reduced. Hence, to fabricate a considerable intermetallic layer on the magnesium alloys by the powder thermal diffusion alloying method in the air, the content of the NH_4Cl powder should be limited in a reasonable region.

Figure 10. (a) The as-diffusion alloyed intermetallic layer obtained with 1 g of NH_4Cl , 10 g of Al powder and 10 g of Al_2O_3 powder as the diffusion source; (b) The intermetallic layer on the specimen which not only underwent the diffusion alloying process in (a) but also underwent another heat treatment at 430 $^{\circ}\text{C}$ for 2 h with 20 g of SiO_2 and 3 g of NH_4Cl in the diffusion source further.

Based on the formation mechanism of the intermetallic coatings on magnesium alloys, the effect of the excess NH_4Cl powder on the intermetallic coatings could be deduced. As the NH_4Cl powder would decompose into NH_3 gas and HCl gas, abundant NH_4Cl powder would result in massive NH_3 gas and excess HCl gas, which would dilute the metallic halide gas and this is not preferred by the diffusion alloying process. Meanwhile, the move of the bulk gases has the potential to cause the mixed powder to vibrate, and some particles would even be blown up. Moreover, excess HCl gas may react with the metallic atoms both in the substrate and in the intermetallic layer and cause erosion. Hence, excess ammonium chloride resulted in a worse intermetallic layer and could even cause material waste, device degradation, and air pollution furthermore.

4. Conclusions

To fabricate a metallic coating on magnesium alloys by the powder thermal diffusion alloying process in the air, the addition of ammonium chloride as an activator in the diffusion source is helpful. The NH_4Cl powder could decompose into NH_3 gas and HCl gas. HCl gas could react with Al powder and produce AlCl_3 gas. The mobility of the AlCl_3 gas is much higher compared to the solid Al powder. Meanwhile, the HCl gas could also turn a dense MgO film into a loose one, which is preferred by the AlCl_3 gas in order to pass through the oxide film and arrive at the magnesium alloy matrix. As a result, the Al-rich intermetallic layer formed on the magnesium alloy substrate.

While the NH_4Cl content should be limited to a reasonable region. Excess ammonium chloride powder could produce a large amount of gas which could dilute the metallic halides, cause vibrating mixed powder and erode the as-formed intermetallic layer. Moreover, excess ammonium chloride powder could also cause material waste, air pollution, and device degradation et al. To utilize the

ammonium chloride powder effectively, it is suggested that the NH_4Cl content should be no more than 10 wt. % of the overall weight of the diffusion source in the diffusion alloying process on the AZ91D magnesium alloy.

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