Deposition Coating of Magnesium Alloys with Pure Magnesium

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Coating on surfaces of magnesium alloy with pure magnesium by applying a retort method to purification and deposition of magnesium has been attempted for improving corrosion resistance. Magnesium with three nine purity was evaporated in a vacuum furnace and deposited on a substrate, AZ31 magnesium alloy, put at a lower temperature zone in the furnace. Elemental conditions for the deposition coating technique have been investigated to obtain homogeneously coated specimens in microstructural and morphological points of view. The coated specimen has shown a superior corrosion resistance compared with uncoated AZ31 alloy.

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1. Introduction

The main disadvantage in magnesium and its alloys is their poor corrosion resistance. Actually, the standard electrode potential of magnesium is lowest among engineering metallic materials. It was reported that the corrosion resistance of magnesium was deteriorated by increasing concentrations of heavy metal impurities such as iron, nickel and copper,¹⁾ therefore, the corrosion rates in magnesium alloys with low concentrations of such impurities less than about few tens mass ppm, were reported to be lower than those in a carbon steel and an aluminum alloy.²⁾ The requirement of extremely low concentrations of impurities makes recycling of magnesium alloys to be complicated and energy-consuming,³⁾ which degrades an ability of recycling for magnesium alloys. An alternative way for improving the corrosion resistance in magnesium alloys is thought to be surface modification by plating,⁴⁾ anodizing treatment,⁵⁾ chemical conversion,⁵⁾ etc. However, when the plated alloys are recycled, the magnesium alloys are contaminated with nickel and copper used for plating, such heavy metals have deteriorative effect on corrosion resistance as mentioned above. On the other hand, chromium oxides used in processes for anodizing and chemical treatment should be restricted to use from the view point of toxicity. The present authors have attempted to coat magnesium alloys with high purity magnesium by applying vapor deposition technique, and the preliminary results have been previously reported.⁶⁻¹¹⁾

In the present paper, fundamental conditions for vapor deposition of magnesium and the main results in corrosion resistance are described.

2. Experimental Procedures

Schematic illustration of a furnace used is shown in Fig. 1. Inner sizes of a stainless steel tube were about 900 mm in length and 30 mm in inner diameter. Change in vapor pressure with temperature and difference in those among metallic elements would be utilized in principle to fabricate deposition coated specimens in the present technique. So estimation of adequate temperatures for evaporation and deposition is nec-

Fig. 1 Schematic illustration of a furnace for deposition coating (a) and temperature profiles (b).

essary. Vapor pressure, P [Pa], of magnesium changes depending on temperature, T [K], as described by the following equation:¹²⁾

$$\log P = -7750/T - 0.855 \log T + 13.53. \quad (1)$$

Mass, w , of magnesium contained in a vapor with 1 m^3 in volume at T and P is simply calculated as:

$$w = M \cdot P / R \cdot T, \quad (2)$$

where M is a molar mass of magnesium and R is a gas constant. Equation (2) gives values for mass of magnesium in vapor at 900 and 500 K as 0.75 g and 0.27 μg , respectively, which recommends that the evaporation source is heated at temperatures around the melting point of magnesium, and the substrate plate is held at temperature around 500 K. However, it is expected that the deposition behavior strongly depends on a temperature profile in the furnace, so the furnace has five heating zones as shown in Fig. 1(a). Various temperature profiles are schematically shown in Fig. 1(b). In the present study, the double-peaks profile "C" was mainly used.

For an evaporation source, 3N-Mg or AZ91E alloy with about 4.5 g in weight was used, while for a substrate plate,

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Table 1 Chemical compositions of alloys (mass%).

	Al	Zn	Mn	Si	Cu	Ni	Fe	Mg
3N-Mg	0.004	0.003	0.004	0.005	< 0.001	< 0.001	0.002	99.5
AZ31	2.51	0.84	0.003	0.003	0.001	—	0.004	bal.
AZ91E	8.1	0.6	0.25	0.03	0.003	< 0.001	0.003	bal.

Table 2 Impurities in 6N-Mg (mass ppm).

Si	S	F	Cd	Pb	Al, Fe, Cu	Cl, Ca, Cr, Mn, Sb	Li, Na, K, As, Ag
0.25	0.18	0.02	< 0.5	< 0.2	< 0.1	< 0.05	< 0.01

Fig. 2 Appearances of deposition coated specimens under evacuated and closed condition: (a) and (b), and under continuously evacuating condition: (c). Temperatures of evaporation sources for all the specimens were 1053 K. Substrates were held at 833, 733 and 625 K for (a), (b) and (c), respectively.

Fig. 3 Deposition coated specimens prepared at 1.5×10^{-3} Pa (a) and at about 1–0.1 Pa (b). Temperatures of the evaporation source and the substrates were 946 and 625 K, respectively.

AZ31 alloy with about $10 \times 10 \times 6$ (mm³) in size was used. Chemical compositions of the alloys are listed in Table 1. The AZ31 alloy was not a commercial one, so the concentration of manganese was low.

In order to evaluate corrosion resistance, salt immersion tests using 1%NaCl solution were carried out on the deposition coated AZ31 alloy, uncoated magnesium and magnesium alloys listed in Table 1 and also a high purity 6N-Mg was examined for comparison. The impurity contents in the 6N-Mg are shown in Table 2. The NaCl solution was not buffered, so pH value was increased during immersion test from about 6.5 at the beginning to about 9.5 after about 350 ks.

3. Results

In order to establish preliminarily the conditions for deposition, the effect of evacuating was firstly examined. A substrate and a evaporation source were put in the furnace, evacuated at about 5×10^{-2} Pa and then closed the valve for evacuating, which was followed by heating at 833 and 1053 K for the substrate and the evaporation source, respectively, for about 9 ks, then air cooled. The fabricated specimen is shown in Fig. 2(a). Crystal growth on the substrate considerably occurred toward the evaporation source side. When the substrate

temperature was decreased at 733 K, the crystal growth was suppressed as shown in Fig. 2(b), but there can be seen uncoated regions. At temperatures lower than 733 K, the wider uncoated regions were remained on the surface of the substrate. While, when the furnace was continuously evacuated during evaporation and deposition process, the condition of deposition was changed, the adequate temperature of substrate became to be low. At the same evaporation temperature, 1053 K, surfaces of a substrate could be homogeneously covered by deposited granular grains of magnesium as shown in Fig. 2(c), except an opposite side surface to the evaporation source. Continuous evacuating seems to be appropriate for deposition coating.

In the case of the specimen shown in Fig. 2(c), the furnace was evacuated using a diffusion pump at about 1×10^{-3} Pa, which was the general evacuating condition in the present study. When the furnace is evacuated by only a rotary pump, a degree of vacuum is estimated about 0.1 to 1 Pa which seems to be a practical condition in manufacturing. In such a condition, deposition coating could be accomplished at the same substrate temperature to that for diffusion pumping. An example of microstructure of the deposited magnesium is shown in Fig. 3(b), together with (a) which was obtained under diffusion pumping condition, for comparison. Morphology and

Fig. 4 Microstructures of coated surfaces at the positions indicated by the schematic illustration. Temperatures of the evaporation source and substrate were 973 and 628 K, respectively.

sizes of the magnesium grains in both cases are resemble one another. Rotary pumping sufficiently gives deposition coated surfaces for magnesium alloys, though a diffusion pump was used in the present study to prevent oxidation of the deposited surface for examining corrosion resistance in the next step.

Temperature profiles also affected deposition. In the case of the specimens shown in Figs. 2 and 3, the temperature profile "A" and "B" in Fig. 1(b) were applied, respectively. In a profile "B", the substrate was put at relatively flat region in temperature gradient. Deposition coating with varying temperature at the flat region was attempted, but the opposite side surface was not coated. And also the profile "A" was not suitable for obtaining a homogeneously coated specimen. When the profile "C" in Fig. 1(b) was applied for deposition coating, the opposite side surface to the evaporation sources could be coated. Figure 4 shows the microstructures of the deposited surfaces at the following portions: the side surface faced to

the evaporation source (a), the top surface (b) and (c), the side surface parallel to longitudinal direction of the furnace (d) and (e), and the side surface opposite to the evaporation source (f). The portions (b) and (d) are nearer than those (c) and (e) on each the surface. The opposite side surface was completely covered with granular magnesium grains, although grain sizes are smaller than those on the other surfaces.

Deposition is, of course, affected by the substrate temperature as shown in Figs. 2(a) and (b), although deposition coating in this case was carried out in the evacuated and closed furnace. Microstructures of the deposited magnesium obtained at the temperature range between 487 and 625 K are shown in Fig. 5. At higher temperatures than 625 K, evaporation of a part of the substrate occurred, which can be expected from a simple calculation using the eq. (1), that is, the vapor pressures of magnesium at 625, 650 and 700 K are about 5.5×10^{-2} , 1.6×10^{-1} and 1.1 Pa, respectively. On the

Fig. 5 Deposition coated specimens prepared at various substrate temperatures. (a): 625 K, (b): 591 K, (c): 573 K, (d): 552 K, (e): 529 K, (f): 487 K.

other hand, at lower temperature than this range, a part of the surfaces were not covered with the deposited magnesium, in such a case, deposition of magnesium occurred on the stainless steel sleeve (see Fig. 1) suffered at higher temperature than the substrate. Grain size of granular magnesium tends to increase with increasing the substrate temperature. Surface undulation seems to be large in the specimens prepared at 573 K (c). Facetted surfaces appear at (a), (b) and (f), which were prepared at 625, 591 and 487 K, respectively. In Fig. 5, only the side surfaces faced to the evaporation source are focused in order to clarify the relationships between the substrate temperature and the microstructures of the deposition coated surfaces. The opposite side surfaces to the evaporation source were difficult to be coated at lower substrate temperatures. While at higher substrate temperature, evaporation of the substrate occurs as mentioned above. So, the substrate temperatures of around 600 K is believed to be appropriate for deposition coating.

Deposition coated specimens prepared at the substrate temperature of 625 K with varying temperatures for the evaporation source are shown in Fig. 6. Both morphologies of surfaces in the specimens fabricated at evaporation temperatures of 873 and 973 K are similar. However, on the specimen (c), which was fabricated at evaporation temperature of 1023 K, small bright particles can be seen. These contrasts were observed as an edge effect of small magnesium particles. From

a view point of homogeneity in microstructure, temperatures of 873 to 973 K are believed to be appropriate conditions for evaporation.

In all the above mentioned results, 3N-Mg was used for an evaporation source. In the practical cases, however, magnesium alloys are considered to be used for evaporation sources. Therefore, AZ91E alloy was attempted to be utilized as an evaporation source. In Fig. 7(a) and (b), microstructures of coated specimen with using 3N-Mg and AZ91E alloy, respectively, for the evaporation sources were shown. Temperatures of substrates and evaporation sources were same at 623 and 973 K, respectively. When the AZ91E alloy was used, the number of grains having facetted surfaces decreased and the surface was seemed to be flattened (b) in comparison with those in the specimen fabricated with 3N-Mg as an evaporation source (a).

The appropriate conditions for deposition coating obtained in the present investigations are the followings: the substrate temperatures are in the range of 590 to 625 K, the temperature range for the evaporation source is between 870 to 970 K and the furnace is to be continuously evacuated at 1 to 10^{-3} Pa. Although evaporation time was changed in the range of 1.8 to 9.0 ks, the results of which was not shown here, it was confirmed that the evaporation source of 3N-Mg with 4.5 g was almost evaporated for about 3.6 ks.

The thickness of the deposition coated layer varied depend-

Fig. 6 Deposition coated specimens prepared with different temperatures for evaporation source: 873 K (a), 973 K (b) and 1023 K (c).

Fig. 7 Deposition coated specimens with using 3N-Mg (a) and AZ91E alloy (b) for evaporation sources. Substrate temperature was 623 K.

Table 3 Mass losses after 260 ks in 1%NaCl solution (mg/m²).

Uncoated AZ31	Deposition coated AZ31	6N-Mg
1053	70	23

ing on the direction of the surfaces. That is, in the specimen prepared at the appropriate conditions, thickness of the surface faced to the evaporation source was in the range of 20 to 50 μm , while the thickness on the opposite side surface was about 5 to 10 μm . Therefore, mass losses of the deposition coated AZ31 alloy in salt immersion tests using 1%NaCl solution with 1 L under stirring condition were measured on the surface faced to the evaporation source with about 160 mm² in area, other side of which were masked with an organic resin. Mass losses in uncoated AZ31 alloy and 6N-Mg were also measured for comparison, the areas were about 810 and 350 mm², respectively. Mass losses after immersion test after about 260 ks are listed in Table 3. The mass loss in the AZ31 alloy was decreased by about a factor of ten by deposition coating to be close to that for 6N-Mg.

4. Discussion

The present deposition coating method resembles to a retort method used for refining magnesium. Inoue *et al.* reported that iron, copper and nickel contents in commercial grade pure magnesium could be decreased into several mass ppm by refining with a retort method.¹³⁾ Deteriorative effects of these elements on corrosion resistance are reported by Hanawalt *et al.*¹⁾ as previously mentioned. The improvement in corrosion resistance by deposition coating (Table 3) is believed to be due to such a refining process possessed intrinsically in the present method. Moreover, deposition coated magnesium covers grain boundary segregations, inclusions, precipitates *etc.*, which are included in magnesium alloys and form local cells with the matrix, and leads to improve the corrosion resistance. The appropriate conditions for deposition coating obtained in the present study are those for homogeneous coating without remaining original surfaces.

For the above mentioned purpose, such a process similar to those used for dew point measurements seems to be suitable. However, in the case of applying a dew point measurement, the evacuated and closed system should be held at a condition having a certain vapor pressure of magnesium, in which higher pressure is desirable for the following deposi-

tion process. Higher vapor pressure means higher temperature, which results in occurrence of evaporation of a substrate magnesium alloy. The temperature range for the substrate recommended in the present study is between 590 and 620 K, which corresponds to the magnesium vapor pressures of about $1\text{--}4 \times 10^{-2}$ Pa, that is, evaporation of the substrate is practically neglected.

In the present method, since the system is continuously evacuated, density and distribution of magnesium atoms in the furnace are affected not only by temperature but also by evacuating rate. The double-peaks temperature profile, which seems to be curious at a glance, is considered to play a role for flattening the distribution of magnesium vapor.

Corrosion rate in magnesium decreases with increasing pH value of solution,¹⁴⁾ and pH value is increased with proceeding of corrosion reaction of magnesium.¹⁵⁾ During the salt immersion tests, the pH value of the NaCl solution used for the uncoated AZ31 alloy was believed to be increased more rapidly than that used for the deposition coated AZ31 alloy, because the area for testing in the uncoated AZ31 was larger by a factor of five than the area in the deposition coated specimen. That is, the deposition coated specimen was suffered under a severer condition compared with the uncoated specimen, nevertheless the former showed a superior corrosion resistance.

The advantages of the present technique are as follows: there is less directionality compared with such as ion implantation technique,¹⁶⁾ which enables one to coat samples having complicated shapes, although the thickness of the coated layer varies depending on the direction of surfaces; removing the surface layer is not necessary in recycling process; magnesium scraps can be used as an evaporation source; there is no restriction on heavy metal contamination for the substrate magnesium alloys. This technique is suitable for recycling and save-energy.

5. Summary

In order to improve poor corrosion resistance of magnesium alloys, deposition coating with magnesium onto magnesium alloys have been attempted by applying a retort method. The difficulty in this technique was to accomplish homogeneous coating in microstructural and morphological meanings. The main factor, that is, temperature ranges for substrates, AZ31 magnesium alloy, and for evaporation source,

3N-Mg, were determined. These factors mainly affect sizes and morphologies of the deposited magnesium grains. Completeness in covering surfaces of the substrate with deposited magnesium has been affected by the temperature profile in the furnace. Mass loss in the deposition coated specimen was smaller by a factor of ten in comparison with that in the uncoated AZ31 alloy, which is due to a purification process possessed intrinsically in a retort method.

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