In Situ Laser Microscopy on Corrosion in Deposition Coated Magnesium Alloy

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Corrosion behavior in magnesium coated AZ31 alloy prepared by vapor deposition technique was examined by means of in situ laser microscopic observations in 1% NaCl solution in comparison with those in 3N–Mg, 6N–Mg and uncoated AZ31 alloy. General corrosion and evolution of hydrogen bubbles at stationary points were observed in all the specimens. Filiform corrosion occurred in the AZ31 alloy and in the 3N–Mg, while it did not occur in the 6N–Mg and deposition coated specimen. General corrosion seemed to suppress the evolution of hydrogen bubbles in the 6N–Mg and deposition coated specimen. Superior corrosion resistance in the deposition coated specimen was confirmed, which is comparable to that in the 6N–Mg.

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1. Introduction

Corrosion resistance in magnesium and its alloys is generally recognized to be poor. Hanawalt et al.1) reported that the corrosion resistance in magnesium was accelerated by small amounts of heavy metal impurities, such as iron, nickel and copper, and that the tolerance limits of these elements were 0.017, 0.0005 and 0.1 mass%, respectively. Indeed, high purity magnesium alloy, AZ91E magnesium alloy, shows superior corrosion resistance.2) However, the corrosion resistances in a commercial AZ31 alloy and in a 3N–Mg are not so remarkable,3) notwithstanding the impurity contents in the alloy were lower than the tolerance limits mentioned above, except the nickel contents which was not exactly analyzed but less than 0.001 mass%. Corrosion resistance of magnesium alloys does not depend only on the impurity levels but also on microstructures as reported by Song et al.4) Such methods as salt immersion tests and electrochemical measurements can provide useful results for understanding the corrosion in magnesium alloys, but the information concerned with individual microstructures are not obtained. On the other hand, in electron microscopic observations, neither transmission nor scanning types, magnification is too high, and only dried specimens are applicable. In situ observations using an optical microscopes seems to be appropriate to investigate corrosion behavior during salt immersion test, which were already tried by Hanawalt et al.1) and Song et al.4) But they used conventional optical microscopes, which lead to unfocused images when the corrosion reactions proceed.

In the present study, a confocal laser microscope was used which enables one to obtain just focused images on roughened surfaces, so it is suitable for in situ observations on corrosion.

2. Experimental Procedures

The details for preparing deposition coated specimens are reported in another paper of this special issue and in the previous papers,5)-9) which is briefly explained as follows: a vacuum furnace with five heating zones was used, the inner sizes of which were about φ30 mm in diameter and 900 mm in length; 3N–Mg and AZ31 magnesium alloy were used for an evaporation source and a substrate plate, respectively; they were evacuated at about 2 × 10^-2 Pa; the evaporation source was put in the higher temperature zone, while the substrate was put in the lower temperature zone. The sizes of the substrate were about 10 × 10 × 6 mm^3.

One of the deposition coated specimens used in the present study was prepared at the temperatures of 973 and 625 K for the evaporation source and the substrate, respectively, and the evaporation time was about 3.6 ks. These conditions were appropriate to obtain a homogeneously coated specimen without macroscopic faults, such as pin holes. However, thickness of the coated layer varied in a range of about 5 to 50 µm depending on the direction of surfaces of the substrate, that is, the thickness on a side surface faced to the evaporation source was larger than other surfaces. This side surface was used for in situ observations mentioned latter. While another specimen was prepared at higher substrate temperature and longer evaporation time, about 640 K for 9.0 ks, respectively. Under these conditions, deposited layer with about 1 mm in thickness was formed on the side surface faced to the evaporation source. The surface was polished and used to observe the relationships between microstructures in the deposited layer and corrosion behaviors.

The above-mentioned deposition coated specimens, uncoated AZ31 alloy, 3N–Mg and 6N–Mg were used for in situ observations of corrosion. Surfaces for observations were mechanically polished and finished by cloth rubbing, except one of the coated specimens, other surfaces were masked by an organic resin. The specimens were immersed into 1% NaCl solution with about 30 mL at about 293 K. A confocal laser microscope, ILM15-H, Lasertec Co., was used for in situ observations. The working distances were about 10 to 20 mm depending on the magnification in the range of 50 to 200 times. Corrosion behavior was observed through the solution with 2 to 3 mm in depth. Chemical compositions of the specimens are listed in Tables 1 and 2.

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3. Results

Corrosion behavior in the uncoated AZ31 alloy was shown in Fig. 1, in which the arrows indicate the same position. Significant change was not observed at the early stage in immersion test (a), but the surface became to be gradually darkened from the start of the immersion test for about 3.6 ks. After 4.7 ks, spouting out of fine bubbles suddenly occurred, which was observed like as a dark mist in (b) because the laser beam was scanned for 10 s to take one frame of micrograph. The portions where bubbles were evolved spread out remaining fan-shaped dark traces as shown in (c). Evolution of bubbles was observed at the front the fan, while any reactions at the remaining traces were not observed (c). The origin of the evolution of bubbles was not resolved in observation (a).

The actively corroded region continued to spread out with evolution of bubbles at the front of the region as shown in Fig. 2. In Fig. 2(a), dark sphere contrast, indicated by the arrow A, is observed which is essentially the same bubble as those fine ones looked like a mist, but the former could not easily float from the surface of the specimen. The corrosion started at Fig. 1(b) encountered the other corroded region (b) and (c)). The active corrosion did not proceed to the corroded region but to the uncorroded region (d). Finally the surface of the specimen was covered by the corroded regions.

The reaction of magnesium dissolution in aqueous environments is expressed as follows:10

$$\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \quad (1)$$
$$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2(\text{OH})^- \quad (2)$$
$$\text{Mg}^{2+}2(\text{OH})^- \rightarrow \text{Mg(OH)}_2 \quad (3)$$

The bubbles observed in Figs. 1 and 2 are believed to be hydrogen bubbles evolved by the reaction (2). The morphology of the fan-shaped traces and the phenomena in which the front of the corrosion is active while the remained traces are less active, look like filiform corrosion occurred in painted aluminum alloys.11 The arrows B in Fig. 2(b) and (c) indicate the same position. The details in shapes of the traces are not changed, which shows the less activity in remained traces.

In 3N–Mg, evolution of hydrogen immediately occurred without an incubation period, as shown in Fig. 3. The micrograph (a) was taken in air, before immersion test, while (b) was taken through solution after 240 s in immersion test. Flows of fine hydrogen bubbles are indicated by the arrows A and B, and sphere bubbles are also observed (b). Small inclusions are observed at the origins of the flows of hydrogen bubbles A and B (a). The bubbles C and D are also seemed to be generated at the inclusions on grain boundary, although the origins are hidden by the bubbles in (b). Filiform corrosion was also observed as shown in Fig. 4. The morphology of the filiform corrosion resembles that in AZ31, but there can be seen some directionality parallel to the bright straight contrasts indicated by the arrows (b). These contrasts are believed to be due to twins which were formed by mechanical
polishing. General corrosion which brings about darkening of the surface also occurred, (b) in Figs. 3 and 4.

After 13 ks, the surface of the specimens was covered by filiform corrosion and general corrosion as shown in Fig. 5. The straight line indicated by the arrow is a scratch which was intentionally induced by a steel blade at 4.8 ks in immersion test. Filiform corrosion were observed to occur at the scratch.

In the 6N-Mg, hydrogen evolution immediately occurred in immersion test like as in 3N-Mg, which is shown in Fig. 6. Line contrasts in Fig. 6 are due to twins. At the origin of a flow of fine bubbles, a small defect can be seen as indicated by the arrow in (a). Darkening of the surface due to general corrosion proceeded with time for immersion test as shown in Fig. 7. Evolution of hydrogen seemed to be suppressed by the general corrosion, the bubble observed in (b) and (c) disappeared in the following micrographs (d) and (e). Filiform corrosion was not observed in the 6N-Mg.

Corrosion in the deposition coated specimen was similar to that in the 6N-Mg, immediate evolution of hydrogen bubbles after immersion and general corrosion occurred, which is shown in Fig. 8. Correlations between the microstructure and the corrosion behavior in the deposition coated specimen was difficult to observe clearly in Fig. 8 because of the rough surface of the coated specimen. Polished surface is suitable for such purpose of observations. But in the specimen in Fig. 8, the thickness of the coated layer was about 30 to 50μm. Therefore, a specimen having a thickly coated layer, ~1 mm in thickness, was prepared and the coated surface was polished, then immersion test was carried out, the results of which is shown in Fig. 9. The microstructures in deposition coated layer are not so different from the ordinary ones. Many hydrogen bubbles were observed at the early stage of immersion test (a). The number of bubbles was decreased with proceeding the immersion being accompanied by darkening of the surface due to general corrosion ((b) and (c)). Concentric circle contrasts indicated by the arrows A' and B', for example, in (c) were formerly active positions for evolution of hydrogen bubbles, which are indicated by the arrows A and B in (a). Similar circular contrasts were observed in Figs. 4(b) and 5, which is, therefore, considered to be formerly active points. Filiform corrosion was not observed in the deposition coated specimen.

4. Discussion

The main corrosion behaviors observed in magnesium, deposited magnesium and AZ31 alloy are as follows: general corrosion, evolution of hydrogen bubbles at a stationary point (Type I bubble) and filiform corrosion. The filiform corrosion is also accompanied by evolution of hydrogen bubbles (Type II bubble) only at the fronts.

The general corrosion occurred in all the specimens. There was an incubation period for evolution of Type I bubbles only in the AZ31 alloy. It was reported that corrosion rate was significantly decreased with increasing aluminum contents up to 2 to 4 mass% in magnesium alloys and that aluminum content in corrosion products on Mg-Al alloys formed in salt im-
Corrosion tests was increased with increasing corrosion time.\textsuperscript{13}\) Chemical property of the corrosion products formed by the general corrosion is considered to be changed in magnesium alloys containing aluminum, which increases corrosion resistance for the Type I bubbles in Mg–Al alloys.

The filiform corrosion occurred in the AZ31 alloy and 3N–Mg. Occurrence of the filiform corrosion in the AZ31 alloys is correlated with the high resistance in corrosion products films which act like as protective coating. In general, the filiform corrosion is recognized not to occur in pure magnesium,\textsuperscript{14} but in the present study, 3N–Mg was suffered from the filiform corrosion. On the other hand, in the 6N–Mg and the deposition coated specimen, the filiform corrosion was not observed. Aluminum content in the 3N–Mg is 0.004 mass\%, so it is simply considered that the chemical composition in corrosion products formed in salt immersion test is not so different from that in the 6N–Mg. The number densities of cathodic points, inclusions or segregations consisted of heavy metal impurities, would be higher in the 3N–Mg compared with the 6N–Mg and deposition coated specimen, while in the AZ31 alloy, grain boundary segregation of aluminum provides a cathodic point.\textsuperscript{10} The tolerance limits for heavy metal impurities proposed by Hanawalt et al. would be too high to prevent the filiform corrosion.

Improvement in corrosion resistance by deposition coating in comparison with the uncoated specimen, reported in another paper and the previous paper\textsuperscript{7} is due to the absence of filiform corrosions. It is considered that pH value of solution increases with proceeding of corrosion, which leads to decrease in corrosion rate of magnesium.\textsuperscript{15} This phenomenon

Fig. 3 Corrosion in 3N–Mg. Before immersion test: (a). After immersion in 1\% NaCl solution for 240 s: (b). The arrows A and B indicate the positions of evolution of hydrogen bubbles, A’ and B’.

Fig. 4 Filiform corrosion in 3N–Mg. (a): before immersion test. (b): after immersion for 3.7 ks in 1\% NaCl solution. The arrows show twins.

Fig. 5 Corrosion in 3N–Mg immersed in 1\% NaCl solution for 13 ks. The arrow indicates a scratch intentionally induced at 4.8 ks.
would occur in all the specimens, but in the deposition coated specimen and 6N–Mg, filiform corrosion does not occur, so the corrosion seems to be suppressed.

5. Summary

Corrosion behaviors in 3N–Mg, 6N–Mg, AZ31 alloy and deposition coated AZ31 in immersion test using 1% NaCl solution were in-situ observed by means of a laser microscope. Evolution of hydrogen bubbles occurred in the 3N–Mg, 6N–Mg and the deposition coated specimen. However, the evolution of hydrogen seemed to be suppressed by general corrosion in the 6N–Mg and deposition coated specimen. While, filiform corrosion occurred in 3N–Mg as well as in the AZ31 alloy. It is implied that not only the presence of aluminum in the alloy but also the impurity level affects the occurrence of filiform corrosion. In the deposition coated...
specimen, contents of heavy metals are low due to intrinsically involved retort effect in the process, which results in improvement of corrosion resistance.

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REFERENCES