CORROSION SCIENCE AND TECHNOLOGY, Vol.5, No.6(2006), pp.218~221

Influence of Microstructure on Corrosion Property of Mg-Al-Zn Alloy

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Influence of microstructure on the corrosion property of Mg-Al-Zn alloy was investigated using potentiodynamic polarization experiments, galvanic coupling experiments, and scanning electron microscopy in sodium chloride solutions. Pitting was the most common form of attack in chloride solution, and filiform corrosion was also occurred in AZ91D-T4 alloy. On the contrary, filiform attack in the bulk matrix was predominant corrosion form in AZ91D-T6 alloy, and the number and size of pit were decreased than those of AZ91D-T4 alloy. Galvanic coupling effect between $Mg_{17}Al_{12}$ and matrix was existed, but the propagation of galvanic corrosion was localized only near the $Mg_{17}Al_{12}$ phase in AZ91D-6T alloy. The corrosion resistance of Mg-Al matrix increased with decreasing Al content in the matrix. And, it could be regarded that Al content in the matrix is decreased by precipitation of $Mg_{17}Al_{12}$ during the aging treatment and it decreases the anodic reaction rate of the matrix and galvanic effect in AZ91D-T6 alloy. It could be considered that the composition and microstructure of surface protective layer would be varied by precipitation of $Mg_{17}Al_{12}$ and subsequent decreasing of Al content in the matrix. And it would contribute the corrosion resistance of AZ91D-T6 aging alloy.

Keywords *: magnesium alloy, galvanic corrosion, precipitates, barrier, pitting*

1. Introduction

Although magnesium is the most active metal used in engineering application, magnesium alloys such as Mg-Al and Mg-Al-Zn exhibit good corrosion resistance under regular atmospheric conditions. However they are relatively susceptible to attack by chloride containg environments.[1)-5)] Two primary reasons are considered for the poor corrosion resistance of magnesium alloys: the local action of galvanic microcells between the magnesium matrix and secondary phases of more noble potential, and conditions which hinder the stability of the protective film.[6)-8)]

Recent research has shown that the corrosion resistance of Mg-Al alloy is increased by the precipitation of $Mg_{17}Al_{12}$ phase, which is affected by the heat treatmenet.[2),9),10)] The present investigation was thus mainly concerned with the influences of $Mg_{17}Al_{12}$ precipitates and subsequent matrix composition variation by heat treatment on the corrosion behavior of AZ91D alloy in a chloride solution. Metallurgical examination and electrochemical techniques including galvanic coupling corrosion tests between $Mg_{17}Al_{12}$ phase and matrix composition alloys were used to investigate the relationship between the microstructure and the corrosion behavior of AZ91D alloy in as-cast, T4 and T6 conditions.

2. Experimental method

2.1 Materials and specimen preparation

AZ91D specimens were prepared by casting with commercial purity melt. Mg-3Al and Mg-6Al binary alloys were produced by melting pure magnesium and aluminum under a commercial flux. $Mg_{17}Al_{12}$ compounds were obtained by vacuum hot pressing of 55Mg-45Al powders and subsequent extruding.

The homogenization treatment was performed at 693K for 16h followed by quenching in water. The artificial aging treatment (T6) consisted the T4 treatment followed by precipitation aging at 443K for 48h. It is known that zinc in AZ91D remains in the matrix under T4 and T6 conditions.[2),9)] Instead of Mg-9Al binary alloy AZ91D-T4 specimens were used in this study because AZ91D was

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consisted of fully solid solution state under T4 condition.

2.2 Electrochemical measurement

The electrochemical experiments in this investigation were conducted in an aqueous 5% NaCl solution saturated with $Mg(OH)_2$. Reagents used in this experiment were Anala R grade, and all solutions were prepared from doubly-distilled water. Nitrogen was supplied through the solution for at least 1h before the experiments. Nitrogen was supplied during the experiments. The experiments was accomplished at a temperature of 298K.

Two different types of experiments were carried out. Potentiodynamic polarization experiments with 10 mV/min scan rate and potentiostatic polarization at various potential were carried out. The poteintial was measured against a saturated calomel electrode(SCE), and all potentials refer to this scale. Platinum wire served as the counter electrode.

The second type of experiments, which was referred to as a galvanic coupling corrosion test, were conducted to investigate the galvanic coupling effect of $Mg_{17}Al_{12}$ precipitates with matrix. Mg-3Al, Mg-6Al and AZ91D-T4 (as Mg-9Al) solid solution alloys were used for the matrix composition materials.

2.3 Microstructure and surface morphology analysis

Microstructure of specimens with various heat treatment conditions and morphology of corroded surfaces were investigated by optical microscope and scanning electron microscope. X-ray EDS was used for investigation of precipitates of alloys.

3. Results and discussion

3.1 Microstructure and corrosion potential of as-cast, T4 and T6 alloy

In the as-cast condition, typical dendrite structure could be seen and aluminum was present in two ways. Aluminum precipitated in the form of $Mg_{17}Al_{12}$(β phase) along the grain boundary, and partly in solid solution with the matrix. It was reported that aluminum content of the matrix could vary from a few percent in the bulk to more than 10% in the vicinity of $Mg_{17}Al_{12}$ phase.[2] In the case of homogenization treatment(T4) of cast alloy, the $Mg_{17}Al_{12}$ phase dissolved in the matrix and it exhibited a single-phase solid solution. Globular particle type of intermetallic compound, which was Al-Mn-Fe series intermetallic compound, was also existed. It is known that the size and distribution of primary phases of Al-Mn-Fe compounds are not affected by heat treatment.[2] Aging the AZ91D to the T6 condition, $Mg_{17}Al_{12}$ phase precipitated dis

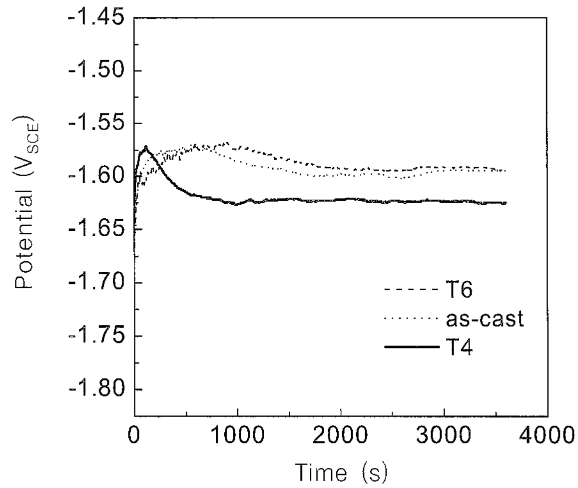

Fig. 1. Variation of the open-circuit potential of AZ91D alloy

continuously along the grain boundary. Al content in matrix was about 3% in the T6 condition.

Fig. 1 shows the variation of open-circuit potential with time of AZ91D alloy in as-cast, T4, and T6 condition. The open-circuit potential increased in order of T4, as-cast, and T6 condition in proportion to the content of $Mg_{17}Al_{12}$ precipitates. Therefore, the differences of open-circuit potential and corrosion behavior of heat treated AZ91D alloys are closely related to the precipitation of $Mg_{17}Al_{12}$ phase and subsequent variation of Al content in the matrix.

3.2 Galvanic effect of $Mg_{17}Al_{12}$ phase

$Mg_{17}Al_{12}$ phases, which had 45% Al content, was precipitated by aging the AZ91D alloy, and Al content in matrix was changed from 9% to 3%. To investigate this aging effect, the open-circuit potentials of Mg-3Al matrix composition alloy and $Mg_{17}Al_{12}$ compounds were observed, and the results are shown in Fig. 2. The open-circuit potential of $Mg_{17}Al_{12}$ compounds was obtained to -1.28 V, and was higher than that of matrix by 0.3 V. It means that the micro-galvanic coupling could be formed between $Mg_{17}Al_{12}$ phase and the matrix in AZ91D-T6 alloy, and $Mg_{17}Al_{12}$ phase serves as a cathode.

To consider the galvanic effect of $Mg_{17}Al_{12}$, galvanic coupling tests were carried out, and the results are shown in Fig. 3. The galvanic current density was about 4 mA/cm^2 when the area ratio of $Mg_{17}Al_{12}$ to Mg-3Al was equivalent. The galvanic current density increased linearly with increasing this area ratio. In AZ91D-T6 alloy, the theoretical maximum volume ratio of $Mg_{17}Al_{12}$ phase is about 15% and the area ratio of $Mg_{17}Al_{12}$ phase in this experiments was measured about 10~11% from the image analysis of microstructure. Hence, galvanic current density at the actual area ratio of $Mg_{17}Al_{12}$ phase was estimated about 0.5 mA/cm^2.

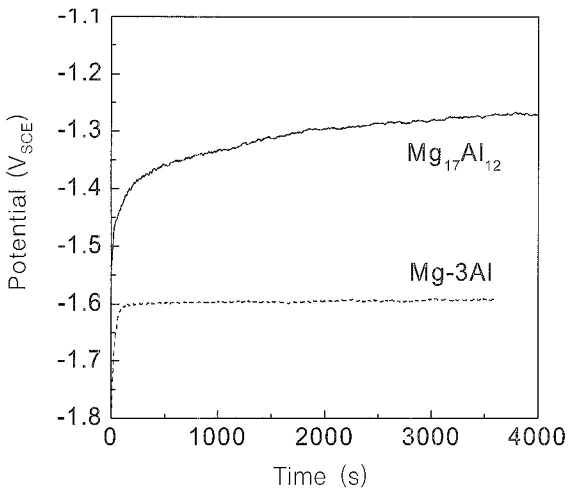

Fig. 2. Variation of the open-circuit potential of $Mg_{17}Al_{12}$ and Mg-3Al

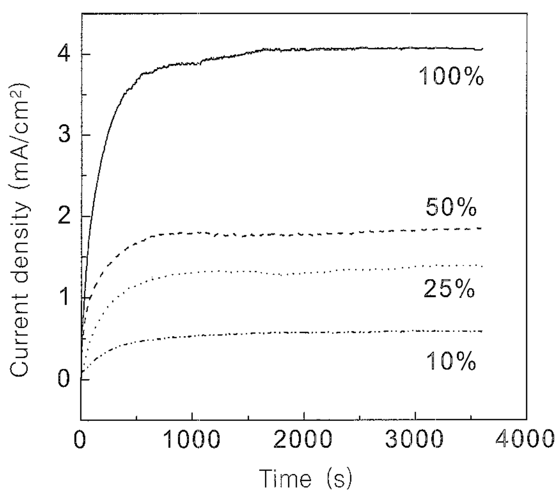

Fig. 3. Variation of galvanic current density with area ratio in Mg-3Al and $Mg_{17}Al_{12}$ galvanic couple

This result shows that the galvanic coupling caused by precipitation $Mg_{17}Al_{12}$ has a harmful effect on the corrosion resistance of alloy. Besides, galvanic current increased with increasing precipitated $Mg_{17}Al_{12}$ phase. But, these are opposite results that the AZ91D-T6 has a better corrosion resistance than the solid solution of AZ91D-T4 which is generally recognized. Lunder et. al.[2)-5)] and Beldjoudi et. al.[9)] explained this conflict as the cathodic activity of $Mg_{17}Al_{12}$ was very small compared to any other cathodic activity such as Al-Mn-Fe compound, and actual effect from galvanic coupling was so small. Also, the cathodic reduction rate of $Mg_{17}Al_{12}$ at near the galvanic potential was relatively small to compare with the anodic reaction rate of Mg-3Al matrix alloy (Fig. 5) in this work. The propagation of corrosion by galvanic coupling was observed by SEM, but the galvanic effect above mentioned was existed only near $Mg_{17}Al_{12}$ phase and filiform type corrosion was observed in the bulk matrix regardless of $Mg_{17}Al_{12}$.

3.3 Effect of Al content in the matrix

In order to investigate the corrosion resistance of the matrix with the variation of Al content, potentiostatic polarization test was carried out for Mg-3Al, Mg-6Al, and AZ91D-T4 (as Mg-9Al). Fig. 4 shows the results of potentiostatic polarization at -1.57 V. As the Al content in alloy decreased, anodic current density decreased and Mg-3Al, which was the matrix composition alloy of AZ91D-T6, showed the lowest value. Besides, the results of the galvanic coupling tests between $Mg_{17}Al_{12}$ compounds and matrix composition alloys indicated that the

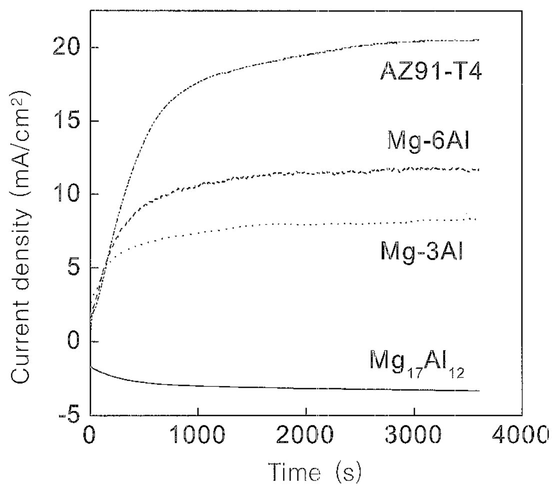

Fig. 4. Current density - time curves for various alloys at an applied potential of -1.57V

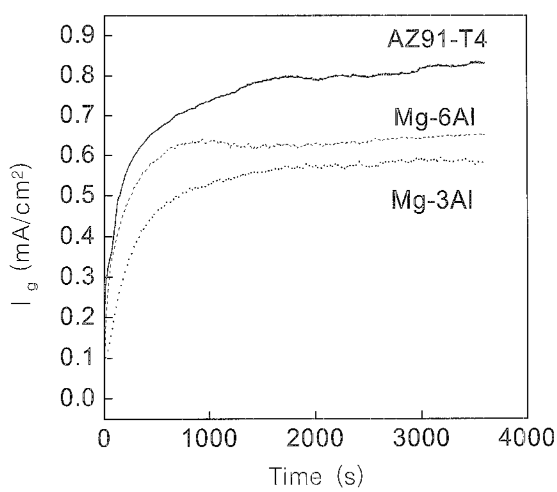

Fig. 5. Galvanic current density in galvanic couples of solid solution alloys and $Mg_{17}Al_{12}$(area ratio 10%)

galvanic current decreased in proportion to the Al content (Fig. 5). Therefore, it follows that Al content in the matrix is decreased by precipitation of $Mg_{17}Al_{12}$ during the aging treatment, and it decreases the anodic reaction rate of the matrix and galvanic effect in AZ91D-T6 alloy.

3.4 Corrosion morphology

Corrosion morphology was observed for the specimens of T4 and T6 conditions by the immersion test and the potentiostatic polarization test. Pitting was the most common form of attack and filiform corrosion was also observed in AZ91D-T4 alloy. On the contrary, in AZ91D-T6 alloy, filiform corrosion in the bulk matrix was predominant, and localized form of attack was existed around the $Mg_{17}Al_{12}$ phase that precipitated along the grain boundary. The number and size of pit in AZ91D-T6 alloy were decreased than those of AZ91D-T4 alloy. From this result and mentioned previous section, it could be considered that the composition and microstructure of surface protective layer would be varied by precipitation of $Mg_{17}Al_{12}$ and subsequent decreasing of Al content in the matrix, and it would contribute the corrosion resistance of AZ91D-T6 aging alloy.

4. Conclusions

1. Pitting was the most common form of attack, and filiform corrosion was also occurred in AZ91D-T4 alloy. On the contrary, in AZ91D-T6 alloy filiform attack in the bulk matrix was predominant corrosion form and the number and size of pit were decreased than those of AZ91D-T4 alloy.

2. Galvanic coupling effect between $Mg_{17}Al_{12}$ and matrix was existed, but the propagation of galvanic corrosion was localized only near the $Mg_{17}Al_{12}$ phase in AZ91D-6T alloy.

3. The corrosion resistance of Mg-Al matrix increased with decreasing Al content in the matrix. And, it could be regarded that Al content in the matrix is decreased by precipitation of $Mg_{17}Al_{12}$ during the aging treatment and it decreases the anodic reaction rate of the matrix and galvanic effect in AZ91D-T6 alloy.

4. It could be considered that the composition and microstructure of surface protective layer would be varied by precipitation of $Mg_{17}Al_{12}$ and subsequent decreasing of Al content in the matrix, and it would contribute the corrosion resistance of AZ91D-T6 aging alloy.

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