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THE ROLE OF $\beta(Al_{12}Mg_{17})$ PHASE ON CORROSION BEHAVIOR OF THE AZ91 ALLOY IN NaCl AQUEOUS SOLUTION

The effect of the β phase ($Al_{12}Mg_{17}$) on the corrosion resistance in a NaCl solution was investigated by electro chemical methods.Volume fraction of β phase in each specimen was controlled systematically by isothermal annealing at 473 K as 0%, 4%, 22% and 100 %, respectively. Although α phase shows lower corrosion current density than that of β phase, the α/β mixed phase specimen showed higher corrosion current density than that of α phase.It strongly suggests that β phase act as cathodic electrode in the alloys.

Keywords: magnesium, corrosion, light alloy

1. Introduction

Magnesium alloys are the lightest among metallic materials used for structural members or machine parts and their application is extending in a broad range of industries. Particularly, transportation industries as typified by the automobile industry have high expectations for weight-critical application to body design aiming for improvement of fuel efficiency. They show the high potential for the aim among practical metals. However, owing to the chemical activity of magnesium alloys, they have been suffered from disadvantages of poorer corrosion resistance than other metals and alloys. Therefor improvement in the corrosion resistance of magnesium is crucial to be employed in actual use environment and several studies on the corrosion resistance have been undertaken. The AZ-series is a turnery alloy of Al, Mg and Zn, having high hope for further expanding application to automobile parts. On the other hand, there is very little information about its corrosion characteristics and there is also a few reports regarding microstructural influence of magnesium on corrosion [1-9]. The β phase ($Al_{12}Mg_{17}$) precipitated by cooling process on casting or during heat treatment in some alloy compositions may result deterioration of corrosion resistance. However, much of its role remains unclear. The influence of the β phase on the corrosion behavior in a NaCl solution was studied in this work. The specimen was Mg-9mass%Al-1mass%Zn alloy and the content of the β phase precipitant was controlled systematically.

2. Specimens and experiments

2.1. Preparation of the specimen

The test material was fabricated by casting to obtain Mg-9mass%Al-1mass%Zn alloy. Mg ingot with industrial purity, pure Al ingot, pure Mn flakes and Al-2.5mass% Be mother alloy were prepared, the latter was cut from ingot to make a final total weight as 400 gf. Pure Mg ingot was melted at 1023 K while fire prevention gas composed of CO_2 and 2%SF_6 was blown to the molten surface. Al ingot was added at the same temperature followed by further addition of pure Mn flakes and Al-2.5mass% Be mother alloy in this order to a predetermined amount while keeping the temperature at 953K. Molten alloy was fed into the casting mold and a Y-shaped casting block was obtained. Specimens with a dimension of 15×12×2 mm were cut from the Y-shaped cast block. The dimension of the Y-shaped cast block is described in Ref. [1]. Solution treated specimens were obtained after heat treatment of solution of 172.8 ks at 703 K on the cast specimens. Three kinds of aging treated specimens were obtained after aging treatment for 2.7 ks, 21.6 ks and 86.4 ks respectively on the solution treated specimens using an oil bath kept at 473 K. A total of four kinds of specimens with different microstructure were prepared for evaluations; the as-cast, the solution treated, the 2.7 ks-aged, the 21.6 ks-aged and the 86.4 ks-aged specimens. Each specimen was plotted on an aging curve shown in Fig. 1. The composition of the specimen is given in Table 1. A 1.029mass% NaCl solution was prepared as the test solution so as to maintain the same anionic concentration of the 2.5mass% Na_2SO_4 solution.

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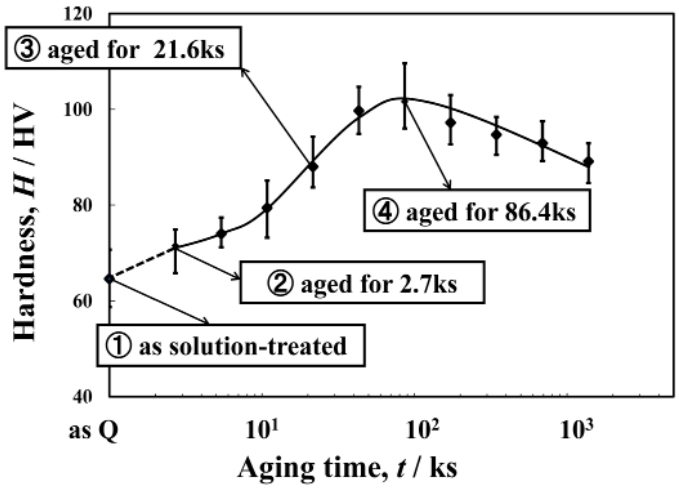

Fig. 1. Aging curve of Mg-9mass%Al-1mass%Zn alloys

TABLE 1

Chemical composition of the AZ91alloy(mass%)

Element	Al	Zn	Mn	Fe	Mg
AZ91	8.78	1.02	0.01	0.002	Bal.

Electrochemical measurements were made for the as-cast, the solution treated, the sub-aged and the peak-aged specimens. The reaction surface of the specimen was polished with fine abrasive papers of 80 to 2000 grades followed by defatting with acetone, cleaning and drying. he surface was coated with silicone rubber for isolation except a reaction area of 1.0×10^{-4} m^2 and used as a test electrode.

2.2. Observation of microstructure using optical microscope

Prepared each specimen was polished with fine abrasive papers of 80 to 2000 grades at first, then buff polished with diamond paste and finally etched. Etching reagent for the as-cast specimens was mixture of 1% nitric acid and 99% ethanol. Mixed solution of picric acid was used for the heat treated specimens. Microstructures were observed with an optical microscope BX51M made by OLYMPUS.

2.3. Polarization curve measurements

A polarization curve was measured for each specimen to investigate electrochemical characteristics of the Mg-9mass%Al-1mass%Zn alloy. An electrolytic cell used for polarization measurements was a H-shaped cell with an internal volume of 4×10^{-4} m^3. The arrangement was a typical three-electrode cell with a specimen electrode having a reaction area of 1.0×10^{-4} m^2 as the working electrode, a Pt counter electrode and a Ag/AgCl (3.33 kmol$\cdot$m^{-3}KCl) electrode as reference. An electrolytic cell kept at 298 K was deaerated by pure N_2 gas flow during 30 minutes. A potentiodynamic scanning was carried out with a rate of 0.5×10^{-3} mVs^{-1} started from near the natural electrode potential (E_{corr}) in potential ranges between –1.6 V and –1.0 V at an anode side. Measured potentials and current densities were recorded after logarithmic conversion. Measurements for Mg alloys were started 1.8 ks after dissolution to equalize initial conditions since the natural electrode potential (E_{corr}) of Mg alloy varies according to dissolution time [10].

2.4. Potentiostatic corrosion tests with constant electric charges

Corrosion morphology after potentiosatic corrosion test was observed for each Mg-9mass%-1mass%Zn alloy specimen. The surface was corroded by a coulombmeter applying a quantity of electricity of 5×10^4 C/m^2 to the reaction surface of 1.0×10^{-4} m^2 while the set potential of each specimen was maintained at E_{corr} + 0.1 V by the potentiostat. After the test, the specimen was cleaned with deionized water, dried in a vacuum desiccator and embedded in a resin. After cutting by high speed cutter, the cut section was polished with fine abrasive papers of 400 to 2000 grades at first, and then buff polished with diamond paste. The cross-sectional microstructure of each specimen was observed by an optical microscope.

3. Results and discussion

3.1. Microstructural observation

Figure 2 shows microstructure of four kinds of specimens; the solution treated, the 2.7 ks-aged, 21.6 ks-aged and the 86.4 ks-aged specimens. The solution treated specimen after heat treatment of solution shows only α phase since the precipitated β phase particles are dissolved into the α phase matrix in full. The 2.7 ks-aged specimen shows cellular precipitants which were consist of lamella $\alpha + \beta$ phase formed along grain boundaries. In the 86.4 ks-aged specimen, specimen surface is occupied with both grown cellular precipitants and intragranular precipitants precipitated within crystal grains. Volume fraction of the β phase; $V_f(\beta)$ were estimated by analysis of the micrographs as 0% for the solution treated, 4% for the 2.7 ks-aged, 22% for the 21.6 ks-aged and 100% for the 86.4 ks-aged specimens when an area of the β phase was considered as a total area of precipitated β phase, cellular precipitants and intragranular precipitation.

3.2. Polarization curve measurements

To investigate the fundamental corrosion behavior, we carried out polarization curve measurements. Anodic polarization curve of each specimen is shown in Fig. 3. All specimens show different profile each other, although they are the same chemical composition. Corrosion potential and corrosion rete of each specimen is listed in Table 2. Corrosion potentials; E_{corr} are

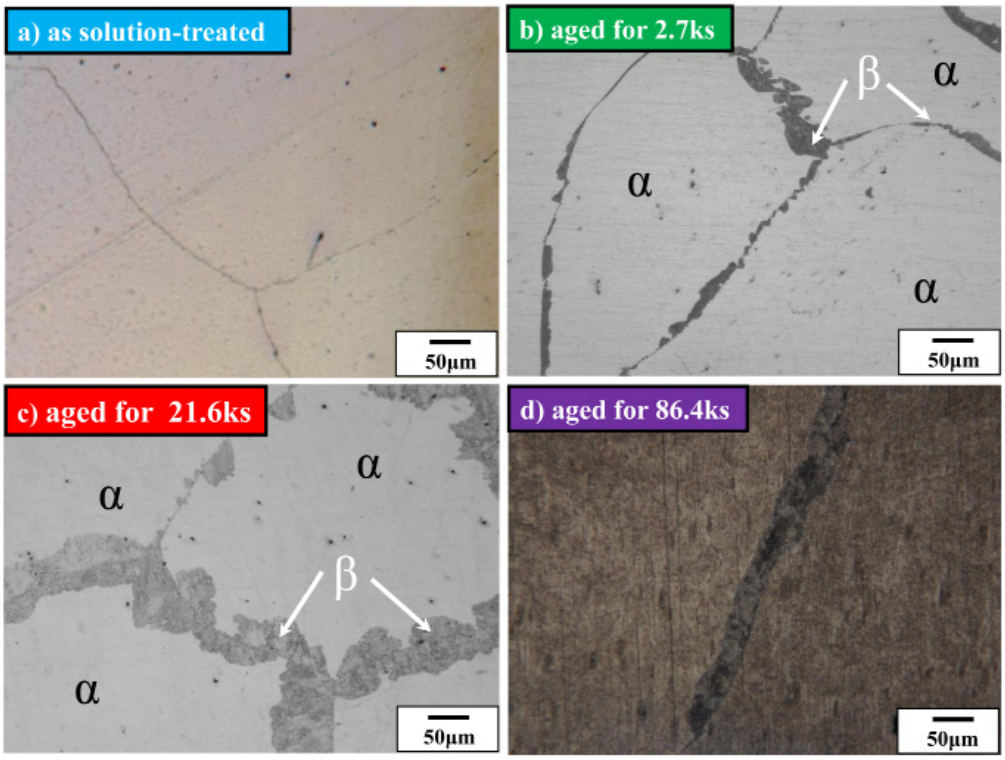

Fig. 2. Microstructure of Mg-9mass%Al-Zn1mass% alloys of (a) solution treated, (b) 2.7 ks-aged, (c) 21.6 ks-aged and (d) 86.4 ks-aged at 473 K, respectively

–1.57 V for the solution treated –1.50 V for the 2.7 ks-aged and –1.47 V for the 21.6 ks-aged and –1.42 V for the 86.4 ks-aged specimens, respectively. It is thought that the Al concentration in α phase control the E_{corr} of each specimen. In the case of α/β mixed phase, Al and Zn are absorbed in β phase. Consequently, E_{corr} of α phase region decrease. It also decreases E_{corr} of the specimen. On the other hand, increase of $V_f(\beta)$ increase E_{corr} of the specimen, due to high E_{corr} of single β phase. In this experiment, E_{corr} increases with the $V_f(\beta)$ because contribution of $V_f(\beta)$ is larger than that of Al and Zn depletion in α phase region. The corrosion current density I_{corr} was calculated for measured polarization curves using the Tafel extrapolation method [11]. Relationship between corrosion current density I_{corr} and volume fraction of the β phase $V_f(\beta)$ is summarized in Table 2. It indicates that the corrosion current density of the solution treated specimens and the the 86.4 ks-aged specimens is relatively low in this study. The result suggests that single α phase have corrosion resistance. However the 2.7 ks-aged and the 21.6 ks-aged specimens show higher corrosion current densities than single α phase. The corrosion current density of α phase (0.12 A/m^2) is lower than that of β phase (0.91 A/m^2). The corrosion current densities of these single phases are clarified quantitatively.

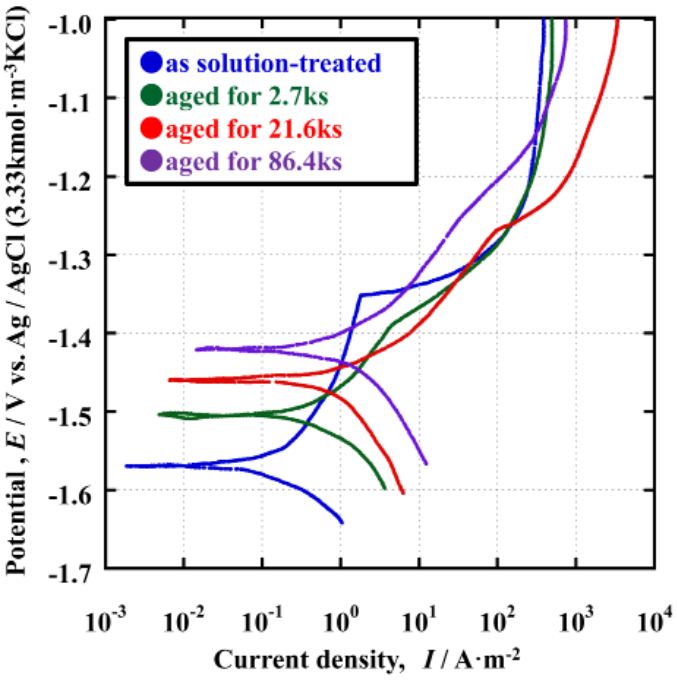

Fig. 3. Anodic polarization curves of AZ91 magnesium alloys measured in 1.029 mass% NaCl solution at 298 K

TABLE 2

Corrosion potential and corrosion current density of each specimen

	As solution-treated ($V_f(\beta)$ = 0%)	Aged for 2.7ks ($V_f(\beta)$ = 4%)	Aged for 21.6ks ($V_f(\beta)$ = 22%)	Aged for 86.4ks ($V_f(\beta)$ = 100%)
Corrosion potential: E_{corr} [V]	–1.57	–1.50	–1.47	–1.42
Corrosion current density : I_{corr} [A/m^2]	0.12	0.39	0.75	0.91

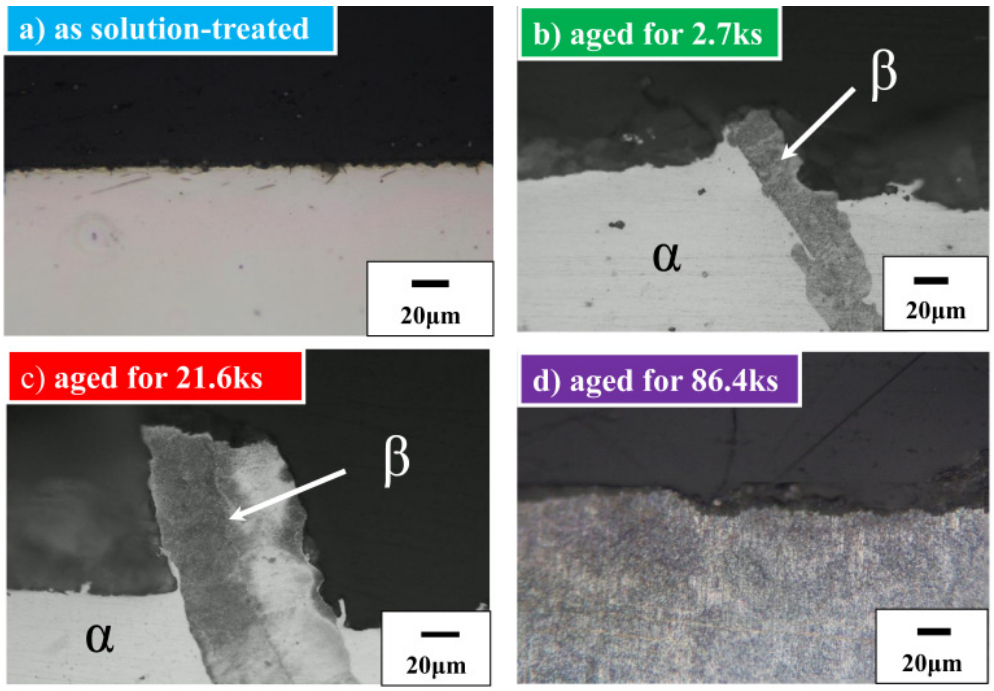

Fig. 4. Micro-structure of the cross-section for the sample Mg-9mass% Al –1mass%Zn in the condition of as cast after 5×10^4 C/m^2 corrosion test in 1.029mass% NaCl solution at 298K.

3.3. Natural electrode potential measurements of 5×10^4 C/m^2 charges

To investigate the reason of the low corrosion current density of specimens which is consist of two phase, we carried out the Natural electrode potential measurements of 5×10^4 C/m^2 charges.

Figure 4 shows cross-sectional surface of Mg-9mass%Al-1mass%Zn alloy corroded with the charge density of 5×10^4 C/m^2. In the cases of α phase (as solution-treated) and the β phase (86.4 ks-aged) surface of the specimens were dissolved homogeneously. While, in the 2.7 ks-aged and the 21.6 ks-aged specimens, α phase appearing white around the β phase dissolves preferentially. However, corrosion current density of β phase is higher than that of α phase in single phase specimens. Therefore, it is strongly suggested that β phase precipitates are act as cathodic electrode to α phase. These results indicate that the single phase of α phase shows corrosion resistant, however mixture of these phase enhance the corrosion because β phase acts as cathodic electrode in the system.

4. Conclusions

From the results of this work, following conclusions have been drawn experimentally.

1. The volume fraction of the β phase influences remarkably on corrosion current density and corrosion resistance in AZ91 alloy. Based on polarization curve measurements, it was extruded that the aged at 473 K for 2.7 ks and 21.6 ks alloy having precipitated β phase shows poor corrosion resistance and the single phase alloy like the solution treated alloy shows excellent corrosion resistance.
2. The corrosion current density of the single phase alloy with the β phase was evaluated first time ever. It was shown quantitatively that its corrosion current density is higher than that of the α phase.
3. Positive correlation between the $V_f(\beta)$ and the corrosion potential E_{corr} suggests that the β phase acts as a cathodic electrode. The results of natural electrode potential measurements of 5×10^4 C/m^2 also supported it.

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