Galvanic Dissolution Behavior of Magnesium–1 mass% manganese–0.5 mass% calcium Alloy Anode for Cathodic Protection in Fresh Water

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Magnesium–1 mass% manganese–0.5 mass% calcium (Mg–1 mass%Mn–0.5 mass%Ca) alloy was used as sacrificial anode. This work was performed to investigate the galvanic dissolution behavior of the alloy anode for cathodic protection in fresh water. The microstructure and dissolved surface of the alloy anode were analyzed with an electron probe micro analyzer, a scanning electron microscope with energy dispersive X-ray spectrometer and a microscope. The current efficiency of the anode has been measured by laboratory test method of galvanic anodes for cathodic protection. It was found that calcium is present uniformly at the grain boundaries as Mg$_2$Ca or Mg–Ca–Si compounds. Calcium compounds dissolve preferentially compared to the matrix of magnesium, as a result the anode uniformly dissolve compared to Mg–1 mass%Mn alloy anode. The current efficiency of the anode for the dissolution was higher than that of Mg–1 mass%Mn anode. On the other hand, manganese is added in order to decrease the local cathode to magnesium alloys, however the part of manganese compounds act as the local cathode in the alloys.

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1. Introduction

The galvanic anode method is a useful corrosion protection of steel structures. Magnesium alloys have been widely applied to the corrosion control of the steel structures in underground and in fresh water, because the potential difference between steel and magnesium alloy is larger than other galvanic anode materials. However, it is well recognized that magnesium alloy anodes have the disadvantage that the current efficiency of electrochemical dissolution is low. Additionally, to the authors knowledge, very little work is available in the published literature on the dissolution mechanism of the anodes. It is therefore important to develop new magnesium anodes of galvanic anode method and to understand the dissolution mechanism of the anodes. The authors developed Mg–1 mass%Mn–0.5 mass%Ca alloy anode by adding calcium of which the potential is lower than magnesium compared to Mg–1 mass%Mn alloy. The purpose of this work is to investigate the galvanic dissolution behavior of the anode in fresh water and the effect of the calcium for the anode.

2. Experimental Procedure

2.1 Materials

Magnesium–1 mass% manganese–0.5 mass% calcium (Mg–1 mass%Mn–0.5 mass%Ca) alloy anode was prepared by casting. After Mg–1 mass%Mn alloy and metallic calcium were melted in a resistance heating furnace at about 720°C under an argon gas atmosphere, molten metal was poured into a mold, followed by slow cooling to room temperature. The elemental analysis for the alloy anode specimens was as follows; Mn: 0.83 to 0.92 mass%, Ca: 0.48 to 0.52 mass%, Al: 0.005 to 0.010 mass%, Fe: 0.002 mass%, Ni: 0.001 mass%, Cu: 0.001 mass%, Si: 0.01 to 0.03 mass%

Potable water was used as a testing solution for the dissolution experiments. The quality analysis of the water was as follows; pH: 7.3, electric conductivity: 230μS/cm, Cl$^-$: 15 mg/dm$^3$, SO$_4^{2-}$: 18 mg/dm$^3$, residual chlorine: 1.1 mg/dm$^3$, total hardness: 73 mg/dm$^3$, Si: 15 mg/dm$^3$.

2.2 Investigation of microstructure and dissolution behavior

The microstructure of the alloy anode specimens was analyzed with a JEOL JXA8800 Electron Probe Micro Analyzer (EPMA), a HITACHI S300N-EMAX7000 Scanning Electron Microscope with Energy Dispersive X-ray Spectrometer (SEM-EDX), and a MAC Science MXP18 X-ray diffractometer (XRD). Schematic diagram of apparatus used for galvanic dissolution test is illustrated in Fig. 1. Prior to the test, the specimen surfaces were finished to a mirror surface with α-alumina paste.

The observing conditions for the galvanostatic dissolution were as follows; temperature: 18 to 23°C, current density: 1.1 A/dm$^2$, and potential: -0.55 V/SCE. The potential was measured against a saturated calomel electrode (SCE) and the current was measured using a copper–coulometer. The current efficiency for the alloy anode was calculated using Faraday's law.

Fig. 1 Apparatus used for galvanic dissolution test.
0.05 to 0.1 mA/cm², flow rate of potable water: 1 to 2 dm³/min. The in situ observation of the specimens was carried out by means of a HIROX KH2700 microscope. The surfaces of specimens after the dissolution test were analyzed with EPMA, and SEM-EDX. The gas evolved from the specimen surfaces was analyzed with a Hewlett-Packard 5890 II gas chromatography.

2.3 Measurement of current efficiency
Prior to the galvanostatic test for measurement of current efficiency, the specimen surfaces were polished down to No. 240 with abrasive clothes. The testing conditions were as follows; solution temperature: 18 to 23°C, current density: 0.1 mA/cm², testing time: 240 hours, Area of anode specimen: 40 cm², flow rate of potable water: 1 to 2 dm³/min.

3. Results and Discussion

3.1 Microstructure and dissolution behavior
The important results obtained in this study are; the precedence dissolution of calcium compounds and the generation of hydrogen gas from manganese compounds. Therefore, we report these points in this order below.

As representative examples, EPMA images of the alloy anode specimen are shown in Fig. 2. Calcium was present uniformly at the grain boundaries as a segregant. Manganese was also present at the grain boundaries. Examination of the grain boundaries with EDX revealed the presence of Ca–Mg, Ca–Mg–Si, Mn, Mn–Fe, Mn–Si, Mn–Fe–Si or Mn–Si–C compounds, etc. Magnesium (Mg) and Mg₂Ca were detected with XRD. These results suggest that the main component of crystal grains and that of grain boundaries are Mg and Mg₂Ca, respectively. All the specimens had grain size of about 0.02 to 0.05 mm. It is assumed that Mg₂Ca compound will be the most active in the alloy specimens. Based on this assumption, we can conclude the followings. The grain boundaries of the alloy anode are electrochemically more active compared to the inside of crystal grains.

Figure 3 is a SEM image of the surface of the specimen after a few minutes of dissolution test. This result indicates that calcium compounds dissolved preferentially compared to magnesium solid solution. The specimens dissolved uniformly afterward, and a smooth film formed on the surface. Calcium compounds do not remain on the specimen surface under the film. These observed results suggest that calcium compounds always dissolved more preferentially compared to Mg, when the specimens are dissolved. These behavior are observed in all the specimens tested. We think that calcium compounds dissolve preferentially, since the compounds show more active potentials compared to Mg.

The specimens uniformly dissolved compared to Mg–1 mass%Mn alloy anodes. It is assumed that this phenomenon is an effect of Ca addition. The local dissolution of the anode specimens is suppressed because the calcium compounds which dissolve preferentially are present uniformly at the grain boundaries. An impurity of silicon (Si) in the alloy anode acts as the local cathode, however the local cell in which Si acts as the cathode is reduced by the generation Ca–Mg–Si compound.

We found that manganese is added in order to decrease the local cathode to magnesium alloy anodes, however the part of manganese compounds act as the local cathode. It was observed that hydrogen gas evolved on the specimens after a few minutes of starting the experiment. The number of the spots where the hydrogen gas evolves increased with increase in the test current density. In order to find the cause of hydrogen generation, a surface analysis was performed. Examination of the specimen surface with EPMA revealed that hydrogen evolves from manganese compounds. The compounds were identified as Mn–Si–C (Fig. 4), Mn–Si, Mn–Fe–Si–C, or Mn–Fe–Si. From these results, it will be concluded that hydrogen gas evolves from the manganese compounds, as a result of local cell action. It is assumed that the formation of the local cell causes decrease in current efficiency.

3.2 Current efficiency
Table 1 shows the results of current efficiency of the specimens in potable water. The result for Mg–1 mass%Mn alloy specimens are also shown for comparison. The current efficiency was 72% on the average, and it was about 10%
higher than that of the Mg–1 mass%Mn alloy specimen. This result suggests that the addition of calcium to Mg–1 mass%Mn alloy is effective. It will be due to the decrease in the local dissolution and local cell.

4. Conclusions

The galvanic dissolution behavior and the current efficiency of Mg–1 mass%Mn–0.5 mass%Ca alloy anode for cathodic protection were investigated in potable water. The following conclusions were derived from the results and discussion.

(1) Calcium is present uniformly at the grain boundaries as Mg$_2$Ca or Mg–Ca–Si compounds. Calcium compounds dissolve preferentially compared to the matrix of magnesium, when the alloy anode is dissolved sacrificially.

(2) The alloy anode uniformly dissolves compared to Mg–1 mass%Mn alloy anode.

(3) The current efficiency of the alloy anode which was measured by short-term test was higher than that of Mg–1 mass%Mn alloy anode.

(4) Manganese is added in order to decrease the local cathode to magnesium alloy anodes, however the part of manganese compounds act as the local cathode in the alloys. The formation of the local cell causes decrease in current efficiency.

REFERENCES


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Fig. 4 EPMA images of the spot where hydrogen gas evolved.