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Fabrication of Mg–Ni–Sn alloys for fast hydrogen generation in seawater

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ABSTRACT

Mg-2.7Ni-x wt.% Sn (x = 0–2) alloys were fabricated to promote hydrogen generation kinetics of Mg-2.7Ni alloy. The Sn in Mg-2.7Ni-Sn alloys exists as Mg₂Sn phase at the grain boundary and solid solution at the Mg matrix. The Mg₂Sn at the grain boundary acts as the initiation site for pitting corrosion and the dissolved Sn in the alloy causes pitting corrosion by locally breaking the surface oxide film in the Mg matrix in seawater. The Mg-2.7Ni-1Sn alloy showed an excellent hydrogen generation rate of 28.71 ml min⁻¹ g⁻¹, which is 1700 times faster than that of pure Mg due to the combined action of galvanic and intergranular corrosion as well as pitting corrosion in seawater. As the solution temperature was increased from 30 to 70 °C, the hydrogen generation rate from the hydrolysis of the Mg-2.7Ni-1Sn alloy was dramatically increased from 34 to 257.3 ml min⁻¹ g⁻¹. The activation energy for the hydrolysis of Mg was calculated to be 43.13 kJ mol⁻¹.

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Introduction

Hydrogen energy has drawn much attention as a future energy source due to its high energy density (120 MJ kg⁻¹), abundant and eco-friendly property [1]. Currently, most of the hydrogen is produced from the combustion of fossil fuels, caused to ejection of CO₂ [2]. Various attempts to develop environmentally-friendly hydrogen generation processes have been reported; hydrolysis of chemical hydrides [3–6] and metallic fuel [7–10], and water electrolysis [11]. Among them, hydrogen generation from the hydrolysis of active metal such as Al and Mg has gained much attention because these active metals are abundant and cheap [12–14]. And the hydrogen

generation system is very simple and easy to control [7–10]. Even though Mg has low H₂ storage density (3.3 wt.%) in water compared to that of Al (3.7 wt.%), it is able to generate hydrogen in neutral solution instead of alkaline solution that is essential to the hydrolysis of Al [10,15–18]. The Mg alloy can be fully recycled by electrical system; its efficiency is calculated to be 41% [19,20]. Hydrolysis of Mg in an aqueous solution can be expressed by Eq. (1) as follows:



Hydrolysis of Mg accompany a formation of passive Mg(OH)₂ layer on the Mg surface (Eq. (1)), which inhibits the hydrolysis of Mg. However, the Mg(OH)₂ layer is readily broken

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by the penetration of Cl^- ions, which lead to pitting corrosion [21–23]. Consequently, the hydrolysis of Mg was maintained continuously in seawater. Powder and bulk types of Mg for hydrogen generation have been studied [24–35]. The Mg powder records high hydrogen generation kinetics; however, it is too dangerous and costly for commercialization.

The bulk Mg, which is economical and safe, records insufficient hydrogen generation kinetics for commercialization [36,37]. Consequently, it has been challenging to develop economical and safe Mg alloys with a fast hydrogen generation rate.

A previous our study [10] showed that a specially designed Mg-2.7Ni alloy exhibited approximately 1300 times faster hydrogen generation kinetics than pure Mg in seawater. An electrochemically noble phase (Mg_2Ni) foamed at the grain boundaries caused galvanic corrosion and intergranular corrosion, which were contributed to the acceleration of the hydrolysis rate.

Based on the previous results [38,39], the addition of Sn to Mg alloy increased the corrosion rate significantly in seawater as a result of accelerated pitting corrosion. The Sn in Mg–Sn alloys may exist as both Mg_2Sn and the solid solution with Mg. The Mg_2Sn in Mg–Sn alloys acts as an initiation site for pitting corrosion [40]. Moreover, the Sn dissolved in the alloy forms tin hydride during hydrolysis which will induce a crevice in the Mg oxide layer through evaporation of tin hydride owing to the low boiling temperature (-52°C). The formation of crevice in Mg oxide accelerated pitting corrosion by attacking of Cl^- ion into crevice [41]. Accordingly, the addition of Sn in the Mg-2.7Ni alloy might enhance the hydrogen generation kinetics of Mg-2.7Ni alloy thorough accelerating pitting corrosion in seawater.

In this work, Mg-2.7Ni-Sn alloys were designed to promote hydrogen generation kinetics of Mg-2.7Ni alloy. And we also examined the surface and microstructure of Mg-2.7Ni-Sn alloys.

Experimental

Fabrication of Mg-2.7Ni-Sn alloys

To design Mg-2.7 wt.% Ni-x wt.% Sn alloys ($x = 0.5-2$), pure magnesium (Mg), nickel (Ni), tin (Sn) were melted at 650°C under protective gas ($\text{CO}_2 + \text{SF}_6$). And then, the fused Mg alloys were cooled in air atmosphere. Based on the previous results [42], to maintain the specially fabricated microstructure of the Mg-2.7Ni alloy, the amount of intermetallic compound (Mg_2Sn) area was controlled by the Sn contents from 0.5 to 2 wt.%. The samples of Mg alloys for the hydrogen generation test were processed into $1 \times 1 \times 0.1 \text{ cm}^3$.

Surface and structural analysis of Mg-2.7Ni-Sn alloys

The scanning electron microscopy (SEM) and back scattered electrons (BSE) were used to analysis surface of Mg-2.7Ni-Sn alloys. And atomic mapping and energy-dispersive spectroscopy (EDS) were used to confirm chemical composition and distribution of Ni and Sn in Mg alloys. Structural information

of Mg-2.7Ni-Sn alloys were confirmed by X-ray diffraction (XRD).

Measurement of the hydrogen generation rate of Mg-2.7Ni-Sn alloys

Hydrogen generation test of Mg-2.7Ni-Sn alloys was employed in 3.5 wt.% NaCl solution at $25-70^\circ\text{C}$. The conical shaped reactor was filled with 75 ml NaCl solution and immersed in water bath to keep temperature stable. The generated hydrogen was detected by a mass flow meter (MFM).

Results and discussion

Microstructures of the Mg–Ni–Sn alloys

Surface morphologies of the Mg-2.7Ni-x wt.% Sn alloys ($x =$ (a) 0, (b) 0.5, (c) 1, and (d) 2) after chemical etching for 3 min in nital etching solution were shown in Fig. 1. It clearly shows that small precipitates were distributed along the grain boundary. And Fig. 1(b)–(d) shows the surface images of the Mg-2.7Ni-Sn alloys. Regardless of the Sn contents, the morphology of the Mg-2.7Ni-Sn alloys was similar to that of Mg-2.7Ni alloy. To confirm the distribution of Sn in the Mg-2.7Ni-Sn alloys, back scattered electron (BSE) image analysis was employed (Fig. 2). Because the contrast of heavy metals is observed brighter than that of light metals in BSE images, the Mg matrix in the Mg-2.7Ni-Sn alloys had the darkest contrast among the three phases shown in Fig. 2(b)–(d). Moreover, the precipitate phases at the grain boundary were slightly brighter than that of the matrix phase which was identified as Mg_2Ni from the previous analysis [10]. Additionally, the brightest phase is probably the Sn phase because Sn is the heaviest among the three metals. The brightest phases seem to be located near the grain boundary, and their contents were increased with the increase of Sn contents shown in Fig. 2(b)–(d). Fig. 3 shows the XRD patterns of Mg-2.7Ni-xSn ($x =$ (a) 0 (pure Mg), (b) 0.5, (c) 1, and (d) 2). For all the Mg-2.7Ni-Sn alloys, Mg_2Ni peaks were clearly observed at $2\theta = 20^\circ-70^\circ$. And except for the Mg-2.7Ni alloy (Fig. 3(a)), the Mg_2Sn peak was also observed at $2\theta = 40^\circ-45^\circ$ [43,44]. Consequently, the brightest phases in the BSE images of the Mg-2.7Ni-Sn alloys were the Mg_2Sn phase. To confirm the distribution of Ni and Sn in the Mg-2.7Ni-1Sn alloys, high resolution atomic mapping analysis was conducted. As shown in Fig. 4, most of the Ni atoms were distributed only in the grain boundary; however, Sn was distributed both grains and grain boundary. To confirm the content of Sn at the grain, EDS analysis was used at the grains of the Mg-2.7Ni-x wt.% Sn alloys ($x = 0.5, 1, 2$). As shown in Table 1, the content of Sn was increased from 0.11 wt.% to 0.52 wt.% with the increase of Sn content from 0.5 to 2 wt.% in the Mg-2.7Ni-Sn alloys.

Hydrogen generation kinetics of the Mg–Ni–Sn alloy

A hydrogen generation test was conducted in a 3.5 wt.% NaCl solution at 25°C to examine the effects of the Sn content of the Mg-2.7Ni-x wt.% Sn alloys ($x = 0.5, 1, 2$) on the hydrogen generation kinetics for hydrolysis. Fig. 5 shows the hydrogen

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