Design of Al–Fe alloys for fast on-board hydrogen production from hydrolysis

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On-board hydrogen production from the hydrolysis of Al in alkaline water has received great attention because it eliminates the need for hydrogen storage. The Al powder, though providing high reaction rate in the hydrolysis, causes a serious problem of explosive danger when in contact with air or moisture, etc. Since the hydrogen generation rate increases linearly with the corrosion rate of Al to Al\(^{3+}\), an Al–Fe alloy, in which an electrochemically noble Al\(_3\)Fe phase precipitates along grain boundaries, is designed, and hence causes fast hydrogen generation from the hydrolysis of Al in alkaline water by combined action of galvanic and intergranular corrosion. The Al alloy containing 1 wt% Fe increases the hydrogen generation rate 3.7 times compared with that of pure Al, in which 65% of the increase is due primarily to the galvanic corrosion between Al and Al\(_3\)Fe phase, and 35% due to the increase in reaction area by intergranular corrosion.

1 Introduction

Hydrogen has received much attention as a future energy source due to its clean, abundant and regenerative properties as well as its high energy density. It is very attractive that the chemical energy of hydrogen can be easily converted to electrical energy using a fuel cell such as a PEMFC (proton exchange membrane fuel cell). Currently, most hydrogen (more than 95%) is produced using a fuel cell such as a PEMFC operated by the hydrogen produced from PEMFC operated by the hydrogen produced from the hydrolysis of Al is recycled into the hydrolysis of aluminium. One kilogram of aluminium generates about 0.110 kg H\(_2\), or 1340 L H\(_2\) (at 1 atm, 298 °C). In the all the previous reports, Al or its alloys in powder forms have been used for the hydrolysis of Al in alkaline solutions due primarily to the large surface area of the powders, leading to the fast reaction rate. However, the powders of Al and Al alloys need to be stored in high vacuum because they are dangerous and explosive when in contact with moisture and air. Further, the Al powders are quite expensive due to complex manufacturing processes. Accordingly, the development of safe Al and Al alloys in such bulk forms as sheet or plate with a high performance of hydrogen generation has proven to be a challenge. It is evident from eqn (1) that the hydrogen generation rate increases in proportional to the corrosion rate or the oxidation rate of Al to Al\(^{3+}\). Accordingly, in order to increase the hydrogen generation rate in the hydrolysis of Al, the corrosion rate of Al should be increased. The corrosion rate of Al would be increased due to the galvanic corrosion and intergranular corrosion in the Al alloy. Among the alloying elements, Fe is very cheap and contained in the range of 1–3 wt% as unwanted material in the wasted Al scraps.

\[
\text{Al} + 3\text{H}_2\text{O} + \text{NaOH} \rightarrow \text{NaAl(OH)}_3 + 3/2\text{H}_2 \quad (2)
\]

\[
\text{NaAl(OH)}_3 \rightarrow \text{NaOH} + \text{Al(OH)}_3 \quad (3)
\]

The hydrogen generation occurs more rapidly in higher concentrated NaOH solution due to the faster dissolution of aluminium hydroxide (Al(OH)\(_3\)) formed on the surface of Al into Al(OH)\(_4^-\) and Al\(_3\)Fe. Alumina has relatively high density of hydrogen storage (3.7 wt% H\(_2\)), and it goes up to 5.5 wt% when the water production from PEMFC operated by the hydrogen produced from the hydrolysis of Al is recycled into the hydrolysis of aluminium. One kilogram of aluminium generates about 0.110 kg H\(_2\), or 1340 L H\(_2\) (at 1 atm, 298 °C). In the all the previous reports, Al or its alloys in powder forms have been used for the hydrolysis of Al in alkaline solutions due primarily to the large surface area of the powders, leading to the fast reaction rate. However, the powders of Al and Al alloys need to be stored in high vacuum because they are dangerous and explosive when in contact with moisture and air. Further, the Al powders are quite expensive due to complex manufacturing processes. Accordingly, the development of safe Al and Al alloys in such bulk forms as sheet or plate with a high performance of hydrogen generation has proven to be a challenge. It is evident from eqn (1) that the hydrogen generation rate increases in proportional to the corrosion rate or the oxidation rate of Al to Al\(^{3+}\). Accordingly, in order to increase the hydrogen generation rate in the hydrolysis of Al, the corrosion rate of Al should be increased. The corrosion rate of Al would be increased by precipitating an electrochemically noble phase such as Al\(_3\)Fe, Al\(_3\)Ni and Al\(_2\)Cu, etc. along the grain boundaries, thereby causing a combined action of galvanic corrosion and intergranular corrosion in the Al alloy. Among the alloying elements, Fe is very cheap and contained in the range of 1–3 wt% as unwanted material in the wasted Al scraps.

\[
\text{Al} + 3\text{H}_2\text{O} + \text{NaOH} \rightarrow \text{NaAl(OH)}_3 + 3/2\text{H}_2 \quad (2)
\]

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\text{NaAl(OH)}_3 \rightarrow \text{NaOH} + \text{Al(OH)}_3 \quad (3)
\]
Accordingly, it is the purpose of the work to design an optimum Al alloy in which an electrochemically noble phase such as Al$_3$Fe is formed along grain boundaries, and hence to increase significantly the hydrogen generation rate from the hydrolysis of the Al alloy by the combined action of intergranular corrosion and galvanic corrosion between the noble phase and the matrix Al.

2 Experimental

Preparation of materials

The Al–Fe alloys (0–6 wt% Fe) designed for fast hydrogen generation were prepared from commercial pure Al (99.9%) and Al–Fe master alloy (Al–50 wt% Fe). The pure Al and the master alloy were melted at 1300 °C to make Al–xFe alloy (x = 1–6 wt %), and then poured into a stainless steel mold, followed by a controlled cooling to room temperature, thereby forming the designed microstructure in which Al–Fe intermetallic compounds such as noble Al–Fe phases are precipitated along the grain boundaries. From the phase diagram of Al–Fe,\(^{20}\) the intermetallic compound is predicted to be Al$_3$Fe, since only Al$_3$Fe compound can be precipitated stably below 20 wt% Fe content in the binary Al and Fe system. The weight contents of Fe in Al–xFe alloys were measured by EDS, and the errors were below 0.1 wt%. The specimens for hydrogen generation were prepared in the form of a cube with 5 × 5 × 5 mm$^3$ by cutting the Al–Fe alloy ingot. The exposed surface area of each specimen was kept constant at 1.5 cm$^2$, with its weight being increased from 0.33 to 0.37 g depending on the Fe content from 0 to 6 wt%.

Analysis

The surface morphology, chemical composition, and microstructure of the Al–Fe alloys were analyzed using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and transmission electron microscopy (TEM), respectively. The polarization response and galvanic corrosion behavior of the Al–Fe alloys were analyzed using a potentiostat/galvanostat with zero resistance ammeter (ZRA).

Measurement of hydrogen generation rate

Hydrogen generation by the hydrolysis of the designed Al–Fe alloys was performed in 50 ml 10 wt% NaOH solution at 30 °C, in which the solution temperature was kept constant by immersing the reactor in a water bath at 30 °C. The volume of hydrogen gas generated from the hydrolysis of the Al alloys was measured by a mass flow meter (MFM). The hydrogen production efficiency (%) was calculated from the ratio of actual H$_2$ production volume to theoretical H$_2$ production volume ($V_{\text{actual}}/V_{\text{theoretical}}$) at a constant temperature of 30 °C and a pressure of 1 atm.

3 Results and discussion

Microstructure of Al–Fe alloys

Fig. 1 shows surface morphologies of pure Al and Al–Fe alloys with various Fe contents that have been subjected to chemical etching for 3 min in 10 wt% NaOH solution. As shown in Fig. 1a, pure Al shows a smoothly dissolved surface with shallow bowls.
Specimen generation rate between Al–1Fe and other alloys is due primarily times higher than that of pure Al. The difference in the hydrogen generation rate of Al–3Fe or Al–6Fe is 2.4 times lower than that of pure Al, whereas the hydrogen generation rate of Al–1Fe is 3.7 times higher than that of pure Al. The above results revealed that the hydrogen generation rate (6.21 ml min⁻¹/C₀) of Al–1Fe was similar to that of the Al–3Fe. The above results revealed that the hydrogen generation rate of Al–1Fe alloy decreased to 1225.6 ml g⁻¹ (efficiency: 91.7%). The hydrogen generation properties of Al–Fe alloys (x = 0, 1, 3, 6) from hydrolysis in 10 wt% NaOH solution at 30 °C: (a) the overall hydrogen generation reaction, and (b) initial (for 20 min) hydrogen generation reaction.

Fe alloys was increased from 0 (pure Al) to 1 wt%, the average hydrogen generation rate increased dramatically from 2.64 ml min⁻¹ cm⁻² to 9.72 ml min⁻¹ cm⁻². However, the average hydrogen generation rate for the Al–3Fe alloy decreased to 6.52 ml min⁻¹ cm⁻², and its total hydrogen generation volume also decreased to 1225.6 ml g⁻¹ (efficiency: 91.7%). The hydrogen generation rate (6.21 ml min⁻¹ cm⁻²) of Al–6Fe was similar to that of the Al–3Fe. The above results revealed that the hydrogen generation rate of Al–1Fe is 3.7 times higher than that of pure Al, whereas the hydrogen generation rate of Al–3Fe or Al–6Fe is 2.4 times higher than that of pure Al. The difference in the hydrogen generation rate between Al–1Fe and other alloys is due primarily to the corrosion behavior of each alloy in the alkaline solution, which will be discussed in detail.

**Galvanic corrosion of Al–Fe alloys during hydrolysis**

Galvanic corrosion occurs when two dissimilar metals with different corrosion potential (Ecorr) are connected electrically in a solution. Then, the electrochemically active metal or that with lower corrosion potential is corroded preferentially while the electrochemically noble metal is protected from corrosion. Furthermore, with increasing the difference in the corrosion potential between two dissimilar metals, the corrosion rate of more active metal increases. Since the corrosion potential of Al is much lower than that of other metals such as Fe, Ni, Cu, Co, and Sn, Al is rapidly corroded when connected galvanically to the other metals in alkaline solution. The galvanic current densities between Al and other metals in a 0.1 M NaOH solution at 30 °C are listed in Table 2. The higher the galvanic current density in the given galvanic couple, the faster the corrosion rate of Al.

On the other hand, the significant increase in the hydrogen generation rate of Al–Fe alloys compared with that of pure Al may result from galvanic corrosion between Al phase and Al₃Fe precipitates. Fig. 4a shows potentiodynamic polarization responses for pure Al and Al₃Fe, respectively, in 0.1 M NaOH solution at 30 °C. It is evident in Fig. 4a that the Al₃Fe phase exhibited a corrosion potential (Ecorr) of −1.12 V SCE that is 0.67 V noble to Ecorr (−1.79 V SCE) of Al. Therefore, the Al phase in the Al–Fe alloy acts as an anode, whereas the Al₃Fe precipitates as a cathode, resulting in an accelerated corrosion of the Al phase in the Al–1Fe alloys. The corrosion current density of Al (icorr(Al)) was measured to be 1.98 mA cm⁻² that is faster than that (icorr(Al₃Fe) = 1.78 mA cm⁻²) of Al₃Fe. Galvanic corrosion tests in the galvanic couple composed of an Al phase and Al₃Fe phase with equal area were conducted using a zero resistance ammeter (ZRA) in 0.1 M NaOH solution at 30 °C. As shown in Fig. 4b, the cathodic current density corresponding to the generation of hydrogen was increased from 1.98 (icorr(Al)) to 4.90 mA cm⁻² (i corr(Al–Al₃Fe)) by galvanic coupling of Al to Al₃Fe that is 2.5 times greater than that of Al without the coupling. It was demonstrated that the hydrogen generation rate of the Al–Fe alloy caused by galvanic corrosion is about 2.5 times faster than that of pure Al, which is almost insensitive to the area ratio of Al phase to Al₃Fe phase in Al–Fe alloys when it is in the range of 1 to 5. The increased ratio (2.5 times) of the cathodic current density in the galvanic couple of Al and Al₃Fe is very similar to that (2.4 times) of the hydrogen generation rate of Al–3 wt% Fe or Al–6 wt% Fe alloys to pure Al as presented in Table 1.

**Intergranular corrosion of Al–Fe alloys during hydrolysis**

As discussed above, it is significant that the hydrogen generation rate (9.72 ml min⁻¹ cm⁻²) of Al–1Fe is much greater than that (6.52 ml min⁻¹ cm⁻²) of Al–3Fe or that (6.21 ml min⁻¹ cm⁻²) of Al–6Fe, that is, 1.5 times greater despite the lower Al₃Fe content of the Al–1Fe alloy. Thus, the greater hydrogen generation rate of the Al–1Fe alloy compared with that of the other alloys is due probably to an intergranular corrosion that may occur only in the Al–1Fe alloy. Fig. 5a clearly shows that intergranular corrosion occurs in Al–1Fe during the hydrolysis reaction, as

![Image](https://via.placeholder.com/150?text=Figure+3)
expected from the microstructure of Al–1Fe where the noble Al$_3$Fe phase is formed along grain boundaries as shown in Fig. 1b. The reason why the intergranular corrosion occurs in the alloy is that the galvanic corrosion of Al (anode) occurs faster at the region nearer to Al$_3$Fe precipitate (cathode) formed along grain boundaries due primarily to the shorter electrical circuit path with lower resistance. Fig. 5b evidently shows that some grains are ejected by the intergranular corrosion, thereby forming a pit with a diameter of 20–30 µm (see Fig. 5c). The pit grows in diameter and depth with hydrolysis reaction of the Al–1Fe alloy in alkaline solution. Evidently, pits grew to those with diameter greater than 100 µm after 10 min hydrolysis as shown in Fig. 6a, and further have increased in number after 20 min, thereby forming a porous structure with large exposed area, as shown in Fig. 6b. It is evident in Fig. 3a and b that the hydrogen generation rate increase in the initial 10 min hydrolysis was due primarily to the increase in reaction area resulting from the intergranular corrosion. However, the hydrogen generation rate was not increased further after 10 min hydrolysis, and was close to a constant value, due probably to the competing effects between the positive effect of the increase in reaction area and the negative effect of the decrease in weight of Al–1Fe specimen with reaction time. In contrast, both Al–3Fe and Al–6Fe alloys subjected to the 10 min hydrolysis show relatively smooth or shallow dissolved surface morphologies without deep pits or intergranular corrosion, as shown in Fig. 7a and b, respectively. The results are expected from their microstructures shown in Fig. 1c and d, where the noble phase, Al$_3$Fe, densely precipitated all over the grains, thereby causing a general corrosion by numerous galvanic corrosion cells. The hydrogen generation rate of Al–3Fe or that of Al–6Fe, shown in Fig. 3b, is 2.4 times higher than that of pure Al, which is close to the increasing ratio of corrosion rate of Al in the Al–Al$_3$Fe galvanic couple with equal area. On the other hand, the hydrogen generation rate of Al–1Fe is 3.7 times higher than that of pure Al (in Fig. 3b) due primarily to the combined effects of galvanic corrosion and intergranular corrosion. Since the effects of galvanic corrosion on the hydrogen generation rate of the Al–1Fe alloy are similar to that of the Al–3Fe or Al–6Fe alloys, that is, about 2.4 times higher than that of pure Al, the effects of intergranular corrosion on the hydrogen generation rate of the Al–1Fe alloy are about 1.3 times higher than that of pure Al.

Table 2 Galvanic current densities between the galvanic couplings of Al–M (Fe, Ni, Cu, C, and Sn) in 0.1 M NaOH solution at 30 °C

<table>
<thead>
<tr>
<th>Metals</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>C</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Galvanic current density with Al/mA cm$^{-2}$</td>
<td>3.72</td>
<td>4.18</td>
<td>1.29</td>
<td>3.09</td>
<td>2.12</td>
</tr>
</tbody>
</table>

Fig. 4 (a) The polarization curve of pure Al (99.9%) and Al$_3$Fe compound at 30 °C in 0.1 M NaOH solution (reference electrode: SCE, counter electrode: Pt, exposed area: Al (0.15 cm$^2$), Al$_3$Fe (0.15 cm$^2$)). (b) The zero resistance ammeter (ZRA) curve for pure Al (99.9%) and Al$_3$Fe compound at 30 °C in 0.1 M NaOH solution for the galvanic corrosion test (exposed area: Al (0.15 cm$^2$), Al$_3$Fe (0.15 cm$^2$)).

Fig. 5 SEM images of Al–1Fe after chemical etching for 5 min in 10 wt% NaOH solution: (a) cracks formed along grain boundaries by intergranular corrosion, (b) separation of grains with a hexagon shape, and (c) the large hole (diameter: 20–30 µm) produced by the separation of grains.
Conclusions

The Al–Fe bulk alloy was designed to form electrochemically noble precipitates along grain boundaries, and hence to cause fast hydrogen generation from the hydrolysis of Al in alkaline water by combined action of galvanic and intergranular corrosion. For the Al–1Fe alloy, a noble phase of needle like Al$_3$Fe precipitates forms along the grain boundaries by a controlled cooling from the melt state. In contrast, for Al–3Fe and Al–6Fe alloys, large amounts of Al$_3$Fe are densely and randomly precipitated all over the grain. The Al$_3$Fe phase in Al–Fe alloys is more noble than the Al matrix, which is confirmed by the difference in corrosion potential between the two phases in 0.1 M NaOH solution at 30 °C; $E_{corr}$ (~1.12 V SCE) of Al$_3$Fe is 0.67 V noble to that (~1.79 V SCE) of Al phase. During hydrolysis of Al–Fe alloys in 10% NaOH solution, the hydrogen generation rate of Al–1Fe was 3.7 times higher than that of pure Al, whereas the rate of generation for the Al–3Fe or Al–6Fe alloys was 2.4 times higher than that of pure Al that is due primarily to the effects of galvanic corrosion between Al$_3$Fe precipitates and Al matrix phase. The excellent hydrogen generation rate of the Al–1Fe alloy results from the combined effects of the intergranular corrosion and galvanic corrosion. The contribution of galvanic corrosion and that of intergranular corrosion were calculated to be 65% and 35%, respectively.

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References