



Effect of Magnesium on Hydrogen Generation Performance of Al-Li Alloy

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The effect of Mg metal on the hydrogen generation performance of Al-Li alloys was elaborated in the present study. The results showed that there existed conflicting effect with increasing Mg content. The grain size of Al-Li alloy was decreased and special surface area was increased therefore with increasing Mg metal, which stimulated Al hydrolysis. But higher Mg metal led to more $Mg(OH)_2$ generation in the hydrolysis process, which covered on Al surface and worsened Al hydrolysis. Our results showed that the side effect of $Mg(OH)_2$ was determine and the hydrogen generation rate of Al-Li alloys was controllable. The reactivity of Al-Li alloys can be regulated *via* changing Mg content. It could be explained that fcc Al(Mg) solid solution and new alloys such as Al_2Mg and Mg_2Al_3 generated in the milling process facilitated uniform mixing of Al and Mg and resulted in more $Mg(OH)_2$ covering Al surface. Therefore, the suitable addition of Mg could reduce the reactivity of Al-Li alloys and presented safe, high hydrogen generation density for micro fuel cell.

Key Words: Hydrogen generation, Hydrolysis kinetic, Aluminum alloy.

INTRODUCTION

Hydrogen is a good fuel for proton exchange membrane fuel cell (PEMFC) where the energy from hydrogen and oxygen is transformed into electricity. Hydrogen powering fuel cell is a good choice for future power source due to the environmental protecting and energy crisis from conventional fuels¹. There still needs to solve the problem of hydrogen storage before the applications of hydrogen for energy purposes. Many hydrogen storage methods still meet some problems such as safety, cost and efficiency and cannot realize the large-scale use of hydrogen². On board hydrogen generation from the reactions of aluminum and its alloys in water or aqueous solutions is recently studied because the method can produce and supply portable hydrogen for fuel cell at anytime where hydrogen is needed. Aluminum and aluminum alloys have many advantages such as low cost (*ca.* 3 dollar/Kg), high theoretic value of 1245 mL hydrogen/1 g Al in alkali solution and cycling. It is a feasible alternative way to supply hydrogen for fuel cells from the waste aluminum in NaOH solution, only consuming water and aluminum. Based on the reaction of aluminum in alkali solution, many hydrogen generators have been designed to supply hydrogen for portable fuel cells³. However, the corrosion of the strong alkali would be a danger to the common user and hinder its practical application as hydrogen sources for portable fuel cells.

Recently, aluminum alloys doped with some metals, such as rare earth metals⁴, alkaline metals⁵ and alkaline earth metals⁶

are considered. These metals can react with water at mild conditions and produce hydrogen and alkaline solution. The alkaline solution further acts as a good catalyst to accelerate aluminum hydrolysis. Among these metals, Li metal is a good choice due to its high theoretic hydrogen generation value (1760 mL hydrogen/1 g Li) and controllable reactivity in water. Lithium can reacts with water gently and its reaction is eventually stopped because of the insoluble lithium hydroxide layer on the metal surface. Al-Li alloys improved the hydrogen generation performance in water at 298 K with increased Li content⁵. However, there still exists a major problem that Al-Li alloy with high lithium content has violently uncontrollable hydrogen generation rate in water. Therefore, finding an additive to reduce the reactivity of Al-Li alloys with high Li content is necessary.

In the present work, Al-Li alloys doped with Mg metal was prepared through the milling method. The hydrolytic properties and microstructures of the alloy were determined. The current study aims to explore the effects of the dopants on Al-Li reactivity and microstructure, elucidate the hydrolytic mechanism of the Al-Li-Mg alloy and to optimize the alloy composition.

EXPERIMENTAL

Al powder (99.9 % purity, *ca.* 10 μ m particle size; Beijing Xingry Technology Company, Ltd., China), Li flakes (99.9 % purity; China Energy Lithium Co. Ltd., China), Mg powder

(99.9 % purity, 280 mesh; Beijing Xingry Technology Company, Ltd., China) were used as starting materials. The reagents were weighed and placed in 50 mL stainless steel jars to which stainless steel balls were added. The jars were kept in an argon-filled glove box. The ball-to-mixture weight ratio was 26:1. Milling was done for 15 h in a QM-3SPO4 planetary ball miller at 450 RPM under a 0.2 MPa argon atmosphere.

Measurement of hydrogen evolution: Hydrolysis was carried out by adding Al-Li-Mg alloy (0.3 g) to water (100 mL) at 298 K and 1 atm. The alloy was pressed into a pellet in a stainless steel mold (10 mm diameter) under 5 tons of pressure before the hydrolysis reaction. The released hydrogen gas flowed through a condenser and its volume was measured *via* water displacement in an inverted cylinder. The reaction time was calculated, with the release of the first bubble as the start of hydrolysis. The final volume of the hydrogen was collected within 1 h of the reaction.

Microstructure analysis: Powder X-ray diffraction (XRD) patterns of the prepared samples were obtained using an X-ray diffractometer (Thermo ARL X'TRA, Switzerland). Scanning electron microscopy (SEM) observations were performed using a JSM-5610LV (JEOL Co., Japan) equipped with an INCA energy dispersive X-ray (EDX) spectrometer. Surface area of the as-prepared samples was measured by a particulate size description analyzer (Dandong Better size, China, specification, BT-2003).

RESULTS AND DISCUSSION

Hydrogen generation from the hydrolysis of milled Al-Li alloys with different Mg content in water was studied. The results are summarized in Table-1 and Fig. 1. Al-20 wt % Li-5 wt % Mg alloy could generate 1359 mL g⁻¹ in pure water at 298 K and 1 atm, with 100 % efficiency. Hydrogen generation of the Al-Li-Mg alloy came from three sources: Al hydrolysis, Li hydrolysis and Mg hydrolysis. Li has high reactivity and can react with water completely. Al hydrolysis and Mg hydrolysis can be stopped when hydrolysis byproduct Al(OH)₃ and Mg(OH)₂ cover their surfaces. The Al(OH)₃ can be removed and Al hydrolysis sustainably occur with increased Li content in Al-Li alloy⁶. But the side effect of Mg(OH)₂ cannot be eliminated and the effect can be increased with increasing Mg content. So it can be seen that Al-20 wt % Li-10 wt % Mg alloy could generate 1280 mL g⁻¹ in pure water at 298 K and 1 atm, with 94 % efficiency. Al-20 wt % Li-15 wt % Mg alloy could generate 1049 mL g⁻¹ in pure water at 298 K and 1 atm, with 77 % efficiency. Al-20 wt % Li-20 wt % Mg alloy could generate 808 mL g⁻¹ in pure water at 298 K and 1 atm, with 59.5 % efficiency. Hydrogen generation rate is

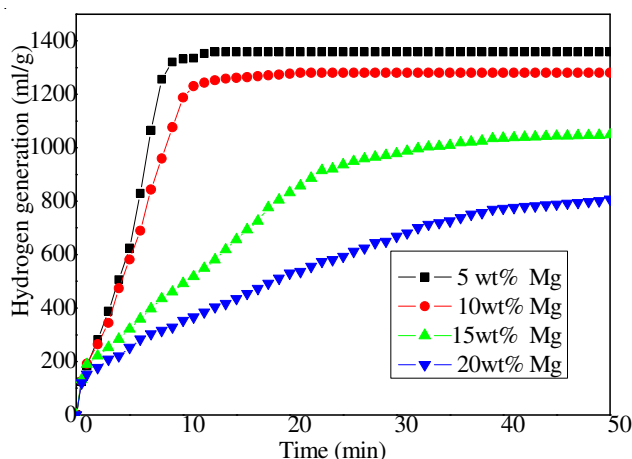


Fig. 1. Hydrogen generation performance of Al-10 wt % Li-x wt % NiCl₂/NaBH₄ mixture (weight ratio, 1:1) at 298 K. x:5, 10, 15, 20

also inversely proportional to Mg content. The hydrogen generation rate of Al-Li alloy within 10 min is decreased from 133 to 49 mL g⁻¹ min⁻¹ with decreasing Mg content from 5 to 20 wt %.

The detailed changes of hydrogen generation rate of the alloy affected by Mg content are shown in Fig. 1. The hydrogen generation curves can be evidently divided into two periods by the inflection point, the former has higher hydrogen generation rate than that of the later. So the two periods can be called to high-hydrogen-generation-rate period (referred to HHGR period) and low-hydrogen-generation-rate period (referred to LHGR period). It can be found that most of the hydrogen generation amount can be obtained in the HHGR period. Al-20 wt % Li-5 wt % Mg alloy can yield 1320 mL g⁻¹ in HHGR period, *ca.* 97 % of the total hydrogen generation amount. Al-20 wt % Li-5 wt % Mg alloy yields 1233 mL g⁻¹ in HHGR period, *ca.* 96 % of the total hydrogen generation amount. The duration of HHGR period is increased with increasing Mg content. Its value increases from 10 to 40 min when Mg content is increased from 5 to 20 wt %. The special surface areas of Al-Li alloy with different Mg content are shown in Table-1. The special surface area increases from 471.45 to 850.46 m² kg⁻¹ when Mg content increases from 5 to 20 wt %.

Fig. 2 shows XRD patterns of milled Al-Li alloys and Al-Li-Mg alloys. The addition of Mg metal has some effects on the microstructure of Al-Li alloys. The peaks of Al-Li, Al or other alloys can be identified in the XRD patterns of Al-Li alloys. With the addition of Mg content, these peaks can also be identified but line becomes broadened, suggesting that the decrease of the grain size and the introduction of lattice during milling intensify. In addition, the patterns of Al-Li-Mg alloys are characterized by the presence of few broad diffraction peaks which can be identified as a nanoscale supersaturated fcc

TABLE-1
HYDROGEN GENERATION VOLUME AND MAXIMUM RATE OF
Al-Li-Mg ALLOY IN PURE WATER AND SPECIFIC SURFACE AREA

Composition design (wt %)	Hydrogen generation rate within 10 min (mL g ⁻¹ min ⁻¹)	Hydrogen generation amount (mL g ⁻¹)	Special surface area (m ² kg ⁻¹)
Al-20 wt % Li-5 wt % Mg	133	1359	471.45
Al-20 wt % Li-10 wt % Mg	119	1280	634.56
Al-20 wt % Li-15 wt % Mg	49	1049	754.40
Al-20 wt % Li-20 wt % Mg	35	808	850.46

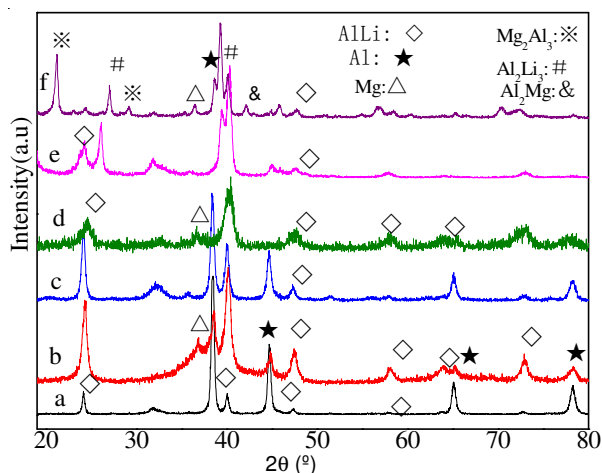


Fig. 2. XRD patterns of milled Al-Li alloys and Al-Li-Mg alloys. (a) Al-10 wt % Li alloy; (b) Al-10 wt % Li-20 wt % Mg alloy; (c) Al-20 wt % Li alloy; (d) Al-20 wt % Li-20 wt % Mg alloy; (e) Al-30 wt % Li alloy; (f) Al-30 wt % Li-20 wt % Mg alloy

Al(Mg) solid solution. A tiny diffraction peak due to residual Mg is visible at 36° . The formation of fcc Al(Mg) solid solution is helpful to prevent the combination of Al-Al, Li-Li and Mg-Mg atoms and increase the split-up of the milled powders. There also exists an interesting result that there are other peaks of Al_2Mg and Mg_2Al_3 which can be identified in the XRD patterns of Al-30 wt % Li-20 wt % Mg alloy. The result is different to previous works⁷. They found that the peaks of Al_2Mg and Mg_2Al_3 were only identified in the melted Al-Mg alloy. Comparison with the XRD patterns of Al-Li alloy and Al-Li-Mg alloy, the peaks of Al-Li becomes stronger, reflected that more Al-Li alloys were formed with the addition of Mg metal.

Fig. 3 shows XRD patterns of hydrolysis by products of Al-Li-Mg alloys. The peaks of $\text{Mg}(\text{OH})_2$ were identified except $\text{LiAl}_2(\text{OH})_7$ hydrate and $\text{Al}(\text{OH})_3$ (bayerite). The lines become broadened with increasing Mg content, reflected that grain size decreases. The results are corresponding to the results in Table-1 and Fig. 2. No peaks of Al are identified, showing that Al has reacted with water completely in a long time. The addition of Mg metal only reduces the hydrogen generation rate of Al-Li alloy, not reducing its hydrogen generation amount.

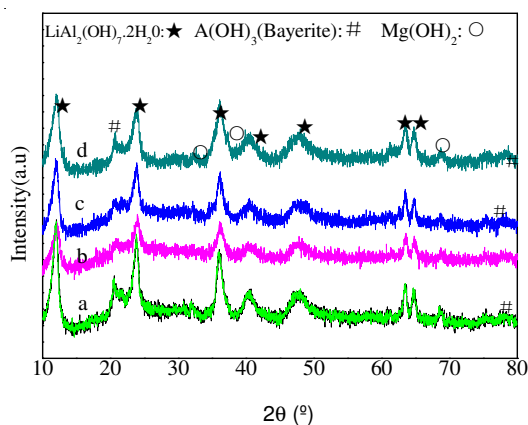


Fig. 3. XRD patterns of hydrolysis byproduct of Al-20 wt % Li alloys with different Mg metal. (a) 5 wt %; (b) 10 wt %; (c) 15 wt % (d) 20 wt %

Fig. 4 shows EDS of Al-Li-Mg alloy after hydrolysis, there are sub-micro platy particles ($\text{LiAl}_2(\text{OH})_7$) and irregular solid [$\text{Mg}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$] in Fig. 4, combined with XRD results in Fig. 3. The solids ($\text{Mg}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$) deposit on the surface of sub-micro platy particles. Due to low solubility of $\text{Mg}(\text{OH})_2$, more $\text{Mg}(\text{OH})_2$ covering Al surface with higher Mg content prevents the contact of Al and water. The hydrolysis of Al-Li alloy includes three periods: Li hydrolysis; Li can react with water to produce hydrogen and LiOH. Catalytic effect of LiOH. LiOH presents alkaline and acts as a catalyst to simulate Al hydrolysis. The reaction of hydrolysis byproduct LiOH and $\text{Al}(\text{OH})_3$. As the presence of Mg element exists in fcc Al(Mg) solid solution and leads to decrease grain size, higher Mg content leads to accelerate Li hydrolysis, but worsens hydrolysis kinetic of Al.

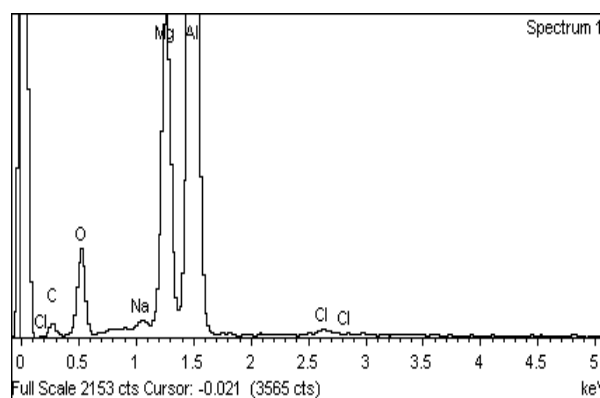


Fig. 4. EDS of Al-Li-Mg alloys after hydrolysis

Conclusion

The current study demonstrates that Mg metal has great effect on hydrogen generation performance of Al-Li alloys. Higher Mg metal leads to more formation of $\text{Mg}(\text{OH})_2$. Hydrolysis by product $\text{Mg}(\text{OH})_2$ covering Al surface prevents the contact of Al and water and worsens the hydrolysis kinetic of Al. Using XRD, SEM and BET analysis, the grain size is decreased and surface area is increased with increasing Mg content therefore, accelerate Al hydrolysis. The hydrogen generation experiments confirmed that the side effect of Mg metal is determined and the hydrogen generation performance of Al-Li alloys is worsened therefore. There is also an interesting result that there are Al_2Mg and Mg_2Al_3 which are firstly found existed in the milled Al-30 wt % Li-20 wt % Mg alloy.

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