

Activation of Al-Li-Ga Alloy and Its Hydrolysis for Portable Hydrogen Sources

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A new process to obtain hydrogen from highly activated Al-Li-Ga alloy in water was described. The milled alloys had good hydrolysis properties especially that the alloy with 12 wt. % Ga produced 1103 mL H₂/1 g Al alloy in 0.5 h of the hydrolysis reaction at 323 K, its efficiency reaching 98 %. From XRD and SEM analysis, the improved hydrolysis properties were explained from the formation of GaLi alloy in the milling process, which acted as initial hydrolysis center and its hydrolysis byproduct LiOH further simulated the corrosion of Al-Ga alloy in water. There existed several micro-galvanic cells between Al-Li-Ga alloy and water, where LiAl₂(OH)₇·2H₂O and Al(OH)₃ (bayerite) were produced with the synergistic effect of Li and Ga. Therefore, this method could be a clean process supplying portable hydrogen source for fuel cell.

Key Words: Hydrogen generation, Aluminum alloy, Portable hydrogen sources.

INTRODUCTION

Hydrogen is regarded as an attractive energy carrier for the future because high efficiently and near-zero-engine-out emissions of hydrogen combustion in fuel cells or hydrogen-fueled internal combustion engines make it potentially applied for mobile tools and vehicles. Its key problems such as generation, storage, transportation and utilization have been extensively researched and have achieved great breakthrough in the applications of hydrogen for energetic purposes. However, hydrogen storage is still urgently to be resolved because many practical methods of hydrogen storages still have some problems of safety, high hydrogen storage value and efficiency. Some potential hydrogen storage methods being developed show highly theoretic hydrogen storage value but still have a long way before the stage of practical application.

On board hydrogen generation may be a good choice as it can supply hydrogen source for fuel cell when and where hydrogen is needed, including natural gas reforming, Bio-derived liquids reforming, photo-electrochemical hydrogen¹. Among these methods, aluminum-water reaction maybe most potentially applied for hydrogen source, because aluminum has low cost (*ca.* 3 dollar/Kg), high theoretic value of 1245 mL hydrogen/1 g Al, low environmental impact, pure hydrogen produced and recycling of its hydrolysis byproduct. Due to alumina oxide film deposited on the solid aluminum surface preventing Al-H₂O reaction, a critical aspect for the reaction is the removal of the oxide layer, using alkali solution or other

metals. For example, Wang² provided a feasible alternative way to supply hydrogen for fuel cells from the waste aluminum in NaOH solution, only consuming water and aluminum as the process was based on aluminum corrosion. However, the corrosion of the alkali would be a danger to the common user and hinder its practical application as hydrogen sources for portable fuel cells. Woodall³ developed a practical portable hydrogen generator, consuming Al-Ga alloy (GaAl₂₈) and water and supplying 6 wt. % hydrogen for fuel cells. In fact, aluminum alloys doped with some metals, such as Ga, Sn, In, Hg, Pb, Bi, Mg or Zn, have a high reactivity and can react with water at mild condition. The hydrolysis mechanism of the aluminum alloy was based on the micro-galvanic cell between the anode (Al), cathode (other metals). In our previous work⁴, the milled some reactive aluminum alloys had a high value of 1000 mL H₂/1 g Al alloy in pure water at room temperature.

Many research work are engaged in improving the hydrolysis properties of aluminum alloys, but so far there has been no attempt to improve the hydrogen storage value as it is well known that the additives such as Bi, Ga, *etc.*, could not react with water and results in the lower hydrogen storage. In this experiment, we choose Al-Li-Ga alloys and investigate their hydrolysis properties at a constant volume of reacting solution of 0.1 dm³ conditions. The purpose of the present work is to provide a new idea to design the aluminum alloys through regulating hydrogen storage value.

EXPERIMENTAL

In order to decrease cost of hydrogen production and hydrogen storage, we used cheap aluminum powder, lithium sheet and gallium as the starting materials. The composites were mixed in an argon-filled glove box. Then ball milling was performed by QM-ISP3 planetary ball miller under a 0.2-0.3 MPa argon atmosphere. Ball-to-powder mass ratio corresponded to 30:1 and the milling time was 15 h.

The hydrolysis properties of Al-Li-Ga alloy were carried out in pure water at 298 K. The weight of Al alloy was 0.3 g and the volume of pure water was 100 mL. The alloy powder was pressed into tablets under 11 ton pressure. At the set temperature, the Al alloys was mixed in water and the produced gas was flowed through a condenser and then was removed by a desiccator prior to measurement of the hydrogen volume. The produced hydrogen volume was measured by monitoring water displaced from a graduated cylinder as the reaction proceeded⁵. Hydrogen yield is defined as the produced hydrogen volume over the theoretical hydrogen volume that should be released, assuming that all material is hydrolyzed. The reaction time was beginning with the first bubble. Powder X-ray diffraction (XRD) studies were carried out on PAN analytical X-ray diffractometer (crystalline silicon is the internal standard). Microstructure studies (EDX analysis) were performed on a CAMEBAX-microbeam electron microprobe equipped with a KEVEX energy-dispersive analyzer.

RESULTS AND DISCUSSION

Fig. 1 shows X-ray patterns of Al-Li-Ga alloy before and after hydrolysis. The peaks of GaLi and AlLi are identified in the X-ray patterns of milled alloys, reflected that new intermetallic compounds were fabricated in the milling process. The broadened line of GaLi alloy becomes stronger and wider with higher Ga content increasing from 3-12 wt. %, companied with the disappearance of AlLi alloy. The results showed that the formation of GaLi alloy is prior to that of AlLi alloy as GaLi alloy had lower Gibbs energy of formation than that of AlLi alloy⁶. Actually, using cauchy/Gaussian approximation according to the calculation method in previous paper⁴, the average crystallite size of aluminum particle (111) also decreases from 230-209 nm roughly and the peak positions shifted slightly, indicative of a change in the lattice parameters as a result of the formation of solid solution with higher Ga content. However, after hydrolysis reaction, all peaks of AlLi, GaLi, Al disappear except those of Ga, replaced by the new peaks of $\text{LiAl}_2(\text{OH})_7 \cdot 2\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$ (bayerite). Fig. 2 shows the SEM morphology of milled Al-Li-Ga alloy before (a) and after (b) hydrolysis reaction. It can be found that the morphology of milled alloys changes from irregular shape to loose "cotton" surface. The irregular shape of milled Al-Li-Ga alloy comes from repeated grain breakup, cold welding and re-welding in the milling process. And the loose hydrolysis byproduct includes "leaf" shape embedded in "cotton" surface. From further analysis, the "leaf" and "cotton" is identified to $\text{LiAl}_2(\text{OH})_7 \cdot 2\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$ (bayerite), respectively.

Fig. 3 shows hydrogen generation curves of Al-10 wt. % Li-X. wt. % Ga alloy (X: 3, 6, 6, 12). It is clear that hydrogen

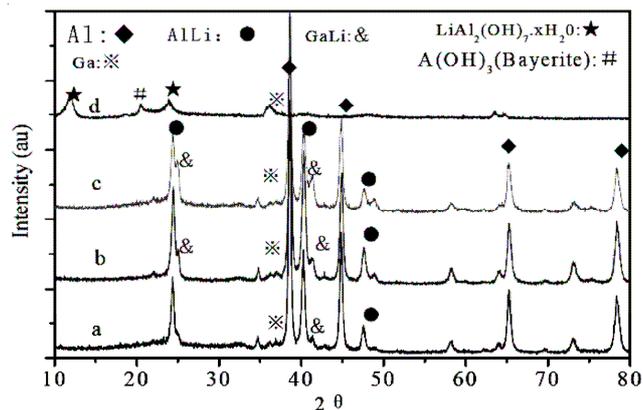


Fig. 1. X-Ray patterns of Al-10 wt. % Li-X wt. % Ga alloy (X: 3, 6, 12) before (a, b, c) and after (d) hydrolysis reaction

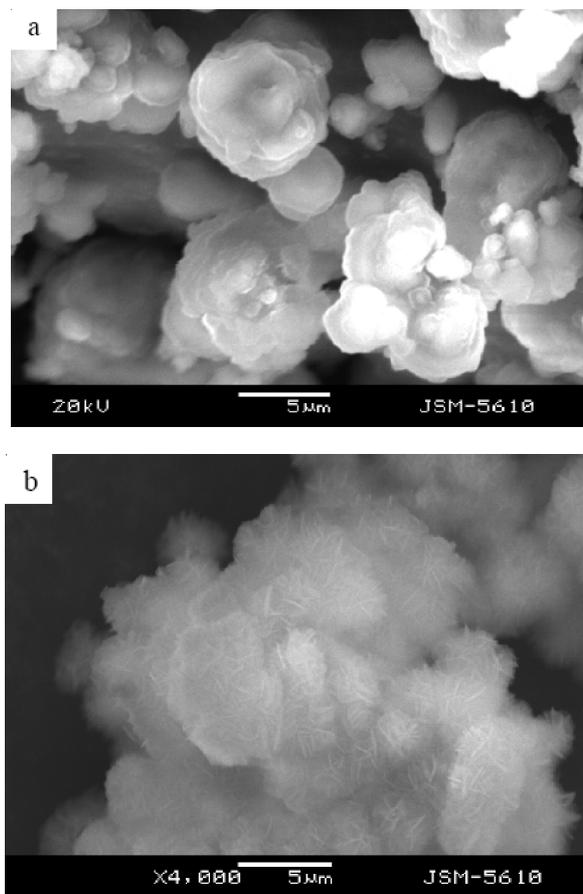


Fig. 2. SEM morphology of Al-Li-Ga alloy before (a) and after (b) hydrolysis reaction

generation amount and rate are increased with higher Ga content. The value of generated hydrogen in 0.5 h hydrolysis reaction is 813, 1001, 1036 and 1103, respectively, using aluminum alloy with 3, 6, 9, 12 wt. % Ga. Their efficiencies are corresponded to 66, 83, 89 and 98 %. Their maximum hydrogen generation rate due to large exposure of the water on the aluminum alloy is 233, 397, 594 and 717 mL hydrogen/min per 1 g, respectively. Obviously, improved hydrolysis properties are attributed to the increased Ga content. Combined with the results in Fig. 1, the intermetallic compounds, especially to GaLi alloy, should be responsible for the improved hydrolysis properties. It has been elaborated that hydrolysis mechanism

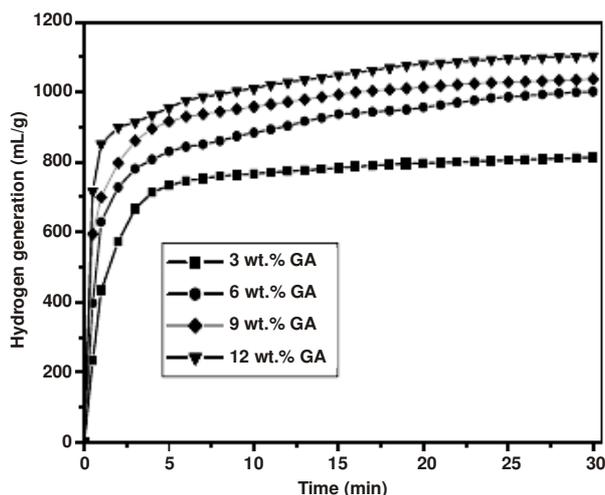


Fig. 3. Hydrogen generation curves of Al-10 wt. % Li-X wt. % Ga alloy

of Al-Ga alloy was based on micro-galvanic cell between anode (Al) and cathode (Ga). But the addition of Li in Al-Ga alloy may simulate the work of micro-galvanic cell and make the hydrolysis process become more complex. In the initial composition of milled Al-Li-Ga alloy, there are the phases of AlLi, GaLi, Al and AlGa. Their standard potential is -1.35, -2.50, -1.67 and -1.13 V, respectively. So AlLi, GaLi and Al can react with water spontaneously because their potentials are lower than -1.29 V of water decomposition, when they contact with water. These reactions may occur according to the followed reaction order: GaLi > Al > AlLi > AlGa, based on the work of micro-galvanic cell. Obviously, GaLi alloy embedded in the Al-Li-Ga alloy can take as the initial hydrolysis center and produce a lot of ions and heat in water in eqn. 1 which also simulates other hydrolysis reaction of Al, AlGa and AlLi. The effect of Ga can be explained to more initial hydrolysis centers generated with higher Ga content. Actually, there exist several micro-galvanic cells between Al-Li-Ga alloy and water and the hydrolysis byproduct LiOH accelerates the work of micro-galvanic cells and changes the hydrolysis process of Al-Ga alloy where AlOOH (boehmite) was produced⁷. The new hydrolysis mechanism can be elaborated according to the followed eqns. 1-3:

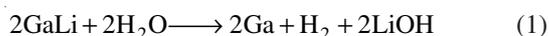


Fig. 4 shows the effect of metal additives on hydrogen generation curves of Al-Li-Ga alloy. Bi additive is helpful to increase the hydrogen generation amount and rate of the alloy, but the other metals reduce the reactivity of Al-Li-Ga alloy, especially that the addition of Zn results in 690 mL hydrogen/g generated in 0.5 h hydrolysis reaction. The difference is mostly explained from the the formation of intermetallic compounds: BiLi₃, Sn₅Li₁₃, GaLi, ZnLi and Mg-Li solid solution.

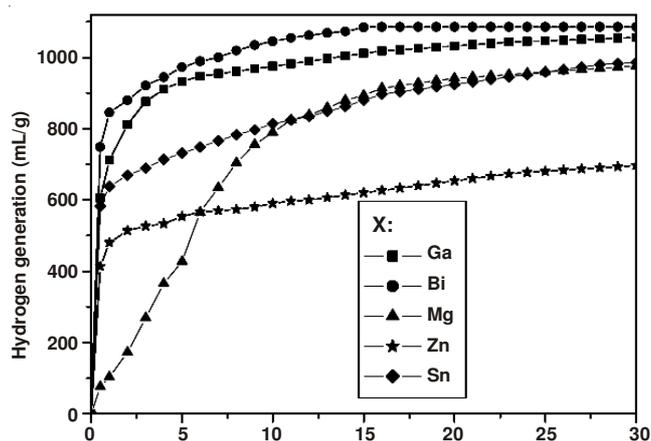


Fig. 4. Effects of metal additives on hydrogen generation curves of Al-10 wt. % Li-6 wt. % Ga-3 wt. % X alloy

Obviously, their ability of improving Al reactivity is corresponding to the followed order: BiLi₃, GaLi, Sn₅Li₁₃, ZnLi and Mg-Li solid solution.

Conclusion

The milled Al-Li-Ga alloys have good hydrolysis properties while approximate 1000 mL hydrogen/1 g Al can be produced in 0.5 h of hydrolysis reaction, with 90 % efficiency. The improved hydrolysis properties are attributed to the synergistic effect of Li and Ga *via* the formation of GaLi alloy in the milling process. GaLi is helpful to improve hydrolysis properties as it takes as initial hydrolysis center and produce hydrolysis byproduct LiOH which simulates the work of micro galvanic cell between Al and Ga. The milled Al-Li-Ga alloys have some advantages of low cost, high hydrogen generation amount, recycling and their hydrolysis byproducts can be separated, so it maybe a potential material supplying portable hydrogen source for fuel cell.

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