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Hydrogen generation by splitting water with Al–Ca alloy

Zhongwei Zhao [a,b,*], Xingyu Chen [a], Mingming Hao [a]

[a] School of Metallurgical Science and Engineering, Central South University, Southern Lushan Street, Changsha 410083, China
[b] Key Laboratory for Metallurgy and Material Processing of Rare Metals, Changsha 410083, China

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ABSTRACT

A new hydrogen generation material, Al–Ca alloy, is prepared by ball milling method. Results show the prepared Al–Ca alloy can react with to produce hydrogen, but its hydrogen yield is lower. NaCl addition can further greatly improve hydrogen generation of Al–Ca alloys. The amount of NaCl addition and ball milling time depends on the Ca contents of alloys. As the Ca contents of alloy increase, the amount of NaCl addition or ball milling time may be reduced accordingly. Increasing Ca contents, NaCl addition or ball milling time is beneficial to improve the hydrogen generation rate. Al–Ca alloys can react with water to produce hydrogen at the temperature ranging from 10 °C to 80 °C, and simultaneously a great amount of heat is released. With the increase of air exposure time, the dense Al_2O_3 and CaO layer formed on the surface of alloy particles will reduce the oxidation reaction rate. Chloride ions and sulfate ions can greatly decrease the induction period of hydrogen generation reaction and obviously improve hydrogen generation rate. Ca^{2+} ions and Mg^{2+} ions can affect the production of hydrogen due to their strong affinity to OH^-, especially Mg^{2+} ions which greatly decrease the hydrogen yield to 20%.

1. Introduction

Fossil fuel depletion and air pollution have become a very serious problem which affect the living and development of Human beings. It is an urgent demand for renewable and clean fuel alternatives for future energy supply [1,2]. Hydrogen is a clean energy carrier with a high calorific value and can store and deliver usable energy [3]. It can be directly used in internal combustion engines or fuel cells [4]. However, hydrogen does not typically exist by itself in nature and must be obtained from some compounds. Some traditional methods of obtaining hydrogen mainly include water electrolysis and fossil fuels decomposition [5]. However, hydrogen produced by above methods must be stored and delivered to users. There are some potential hazards in the process of hydrogen storage and delivery because hydrogen is a kind of flammable and explosive gas. Now, rapid production and safe storage and delivery of hydrogen have become the bottlenecks which hinder the development of hydrogen-based economy [1]. In order to resolve these problems, many new hydrogen generation methods are proposed by researchers. Among these methods, hydrogen generation by the reaction of metal, metal alloy or metal compounds with water is becoming the research focus [6,7], especially using Al and its alloy. Water is the most promising hydrogen production resource due to its high contents of hydrogen [8]. Aluminum, abundant in earth, has low density, high capacity and good activity and is a very potential material for hydrogen generation [9]. So Al will be a very attractive material for energy storage and conversion [10]. In addition, the product of reaction between Al and water is $Al(OH)_3$ or AlOOH which is easily recycled to produce Al by Hall–Heroult process [11].

Although aluminum is one of the most reactive metals thermodynamically, a layer of inert thin film easily forms on its surface and prevents water from contacting with Al metal surface. So aluminum almost does not react with near-neutral pH water solutions [12]. Many measures, such as reacting with alkaline or sodium aluminate solutions and preparing Al alloy or Al-based materials, are adopted to eliminate the inert thin oxide film. In the reaction of Al with alkaline or sodium aluminate solutions, the solution is extremely corrosive and not suitable to produce hydrogen for use in vehicles [13–15]. In order to disrupt the alumina film, Woodall [16] dissolve Al into liquid gallium to prepare Al–Ga alloys. The Al–Ga alloy can rapidly react with water to generate hydrogen. But the content of Ga in earth is much less than other metals, so its price is very expensive. Additionally, Ga does not participate in the hydrogen generation reaction, which will reduce the hydrogen density of unit mass of Al–Ga alloy. Now, mechanical ball milling is used to activate Al by many researchers. Mechanical ball milling method can cause many various defects

* Corresponding author. School of Metallurgical Science and Engineering, Central South University, Southern Lushan Street, Changsha 410083, China. Tel.: +86 731 88830476; fax: +86 731 88830477.
E-mail address: zhaozw@mail.csu.edu.cn (Z. Zhao).

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and create many fresh surfaces by fracturing in metal particles [17]. Many Al-based materials have been researched, such as Al-salt system, Al–Al_2O_3 system and Al alloy or Al alloy-salt system, and so on. For example, some researchers [18] prepare the mixture of Al and NaCl with mole ratio varying from 1 to 7 by ball milling. Only when the NaCl addition reaches 77 wt%, 100% of hydrogen yield can be achieved. And some researchers [5] add $Al(OH)_3$ or Al_2O_3 into Al powders to prepare aluminum metal ceramic by ball milling. As the addition of Al_2O_3 reaches 90%, only about 70% of hydrogen yield is obtained. Although above methods can well disrupt the inert film, the hydrogen production of unit mass is also too low. In addition to above methods, some rare metals, such as Bi, Ga, In and Sn, are added during the process of ball milling Al alloy or Al alloy-salt [19–22]. These rare metals can indeed improve the hydrogen generation of Al powder. However, these metals themselves cannot produce hydrogen, which will also decrease the hydrogen production of unit mass. Additionally, the price of rare metals is very high, and these byproducts are hard to be recycled.

It is necessary to find a metal to activate Al and improve the hydrogen generation. And the metal not only participates in the reaction of hydrogen generation but also has lower price and abundant reserves. Based on above analysis, we find that metal calcium, one of alkaline earth metals, is very suitable to activate Al. In this research, we will prepare a new hydrogen generation material, Al–Ca alloy, by ball milling method. The effect of preparation conditions and reaction conditions on hydrogen generation will be investigated in this paper.

2. Experimental

Al (99.9 wt%, analytical grade, 74 μm), Ca (99.5 wt%, analytical grade, 0.5 mm) and NaCl (99.8 wt%, analytical grade, 140 μm) are used as starting materials. Firstly Al and Ca are melted to prepare Al-75%Ca master alloy by vacuum induction melting. The prepared Al–Ca master alloy is used as materials to prepare the desired Al–Ca alloy with different composition by adding Al or NaCl using ball milling. Ball milling is performed in planetary ball miller (Qm-1SP-2, Nanjing University Instrument Plant, China), equipped with stainless steel milling jars 500 ml and steel balls 4–5 mm in diameter, under argon atmosphere with a ball to powder mass ratio of 10:1. The ball milling time varies from 10 min to 60 min. The rotating speed is kept at 512 rpm during the ball milling. Scanning electron microscope (SEM, JSM-5600, JEOL, Japan) is used to observe the surface morphology of samples.

The hydrogen generation reactions of alloy are carried out in a plastic reactor of 50 ml. In a typical experiment, 0.5 g of alloy powder is placed in the reactor, and then 20 ml of water (salt solution) with different temperatures is charged into the reactor. The generated H_2 flows through a water bath at room temperature in order to cool H_2 gas and to condense the water vapor. The volume of H_2 gas is measured by the water displacement method. The detailed operation is described as follows. H_2 gas is collected in a container filled with water, and water is displaced into a 500 ml flask through a pipe connected with this container. The mass of flask with water displaced by H_2 gas is measured by electronic balance (UX2200H, Shimadzu Corporation, Japan). The electronic balance connects with a computer which can record these mass data automatically. These data can be converted into H_2 volume. In addition, the temperature change curves of Al–Ca alloy reacting with water is determined by thermometric instrument (Victor 86B, Shenzhen VICTOR Hi-Tech Corporation, China) which connect with computer to record temperature data automatically.

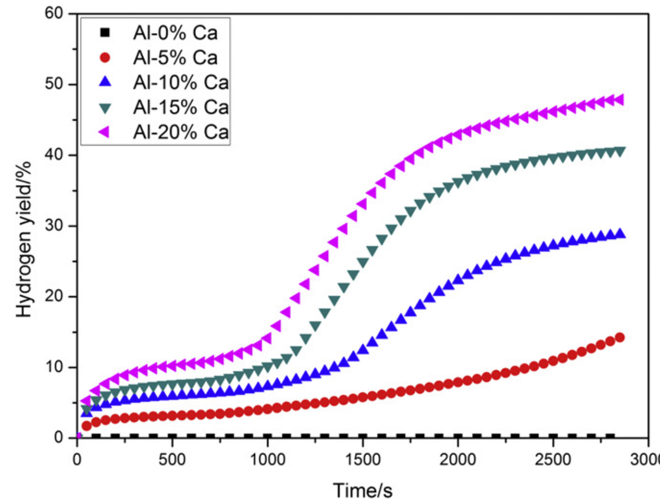

Fig. 1. Hydrogen generation curves of Al–Ca alloy reacting with water.

3. Results and discussion

3.1. Preparation of Al–Ca alloy

3.1.1. Effect of NaCl salt addition

Fig. 1 shows the hydrogen generation yield of Al–Ca alloy with different Ca contents reacting with water at room temperature. From the figure, increasing the Ca contents of alloy can improve the hydrogen generation rate and hydrogen yield. But the hydrogen yield of all samples does not exceed 50% of theoretical yield. When the Ca content reaches 20%, the hydrogen yield is only 47.87% which does not meet with requirement completely. The reason is that the dense calcium oxide and alumina layer easily form on the surface of Al–Ca alloy. The dense layer prevents the reaction of the alloy with water.

In order to activate the Al–Ca alloy and improve hydrogen generation rate and yield, a certain amount of NaCl salt is added into Al–Ca alloy. Fig. 2 is hydrogen generation curves of the reaction between water and Al–Ca alloy with different NaCl addition. Fig. 2a shows the hydrogen generation curves of Al-15%Ca alloy, and Fig. 2b is for Al-20%Ca alloy. The two figures show increasing NaCl addition can remarkably improve the hydrogen generation rate and yield of samples. When the NaCl addition reaches 7%, the hydrogen yield of Al-15%Ca alloy (see Fig. 2a) and Al-20%Ca alloy (see Fig. 2b) can reach 100%. 5%NaCl addition for Al-20%Ca can improve hydrogen yield from about 50% to 96.5% (see Fig. 2b). It indicates that when the Ca content of alloy increases, the NaCl addition may be reduced accordingly, and a high hydrogen yield can still be gained.

In addition, for the reaction of Al–Ca alloy with water, the total process mainly includes three steps. The stage one is induction reaction period, stage two is rapid reaction period and stage three is slow reaction period. Before adding NaCl salt, the former two steps need longer time, which can be seen from Fig. 1. After adding NaCl salt, the time of each stage is reduced. Fig. 2 shows that increasing NaCl addition can effectively cut the induction and rapid reaction period. When 7%NaCl is added, the induction reaction period is reduced from about 1000 to 1100 s to about 500 s (see Fig. 2b). At the same time, the reaction is accelerated obviously. The hydrogen yield is increased from about 10% to 100% in about 300 s.

The addition of NaCl plays an important role in inhibiting the cold welding of Al–Ca alloy and increasing the specific surface area of Al–Ca alloy during the process of ball milling. In addition,