

Generation of Hydrogen through the Hydrolysis of Gas Atomized High Purity Mg Powder

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Generating hydrogen through hydrolysis of metal magnesium with water is a very promising strategy for portable applications because it is clean, has high energy density and operability. In the present study, high purity ultrafine Mg powder was prepared using close-coupled gas atomization. Thereafter, the microstructure of the powder was investigated through X-ray diffraction and scanning electron microscopy. The results showed that increasing the speed of ball milling improved the reaction activity of Mg powder. Moreover, a higher water temperature was shown to be beneficial in improving hydrolysis. Moderate amounts of alcohol in water could also improve the yield of hydrogen.

Keywords: hydrogen generation, hydrolysis, gas atomization, Mg powder.

1. INTRODUCTION

The demand for promising and alternative sources of clean fuel has been on the rise with the depletion of fossil fuel resources and an increase in environmental deterioration. Notably, hydrogen is a carrier of clean energy, with a high calorific value and has therefore gained tremendous popularity in recent research [1]. In addition, to use in fuel cells [2], hydrogen can also be used directly in hydrogen internal combustion engines [3]. However, although hydrogen exists in the atmosphere, the amount is too little. Additionally, many industrial technologies for the production of hydrogen have been invented although most methods are based on the decomposition of fossil fuels [4–6]. Therefore, these methods limit its portable applications, such as use in mobile communication devices, laptops and small electric cars.

Recently, research has largely focused on generating hydrogen from the hydrolysis of metal [7–10]. Compared to conventional techniques, these methods have many advantages including convenience, low cost of raw materials, high theoretical hydrogen yield and high purity [11, 12]. Among the metals, Magnesium (Mg) has attracted the focus of most studies because it has a high hydrogen capacity, low cost, convenient operation and mild reaction. However, the hydrolysis reaction of Mg-based materials is usually blocked by the layer of magnesium hydrate on the surface of the materials [13, 14]. Consequently, several methods have been proposed to overcome this problem, including the ball milling process [15], which is demonstrated to be an effective strategy for improving the

yield of hydrogen. In addition, raising the reaction temperature is proved to be effective in breaking the passive layer [10]. Alloying, additives and ion exchangers are also proved to be useful in reducing the formation of the passive layer [16, 17].

In this study, close-coupled gas atomization was used to prepare high purity ultrafine Mg powder. Notably, the ultrafine powder provided a large surface area that was helpful in enhancing the efficiency of hydrogen production. Additionally, the effects of water temperature, ball milling, alcohol and NaCl on the production of hydrogen were studied.

2. MATERIALS AND METHODS

High purity (99.99 %) Mg was used as the raw material. The raw material was subjected to vacuum induction melting at 990 ± 5 K and atomized in Ar with a pressure of 4.5 MPa. The atomization was performed in a PSI HERMIGA gas atomizer. A schematic diagram of the gas atomizer is shown in Fig. 1. In addition, intermediate frequency induction was used to prepare the high purity melted Mg. Thereafter, the melt was transferred to the atomizer and atomized to be powder. The powder was collected in a collector under the atomization chamber.

The experimental setup used in the hydrogen generation reactions is shown in Fig. 2. The equipment consisted of three sections, one for the reaction, another for regulating the temperature and the third one for measuring the volume of hydrogen. A timer was used to record the reaction time. Notably, the reaction section consisted of a 200 ml gas

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washing bottle where the powder and reaction liquid (distilled water or alcoholic solution) were mixed.

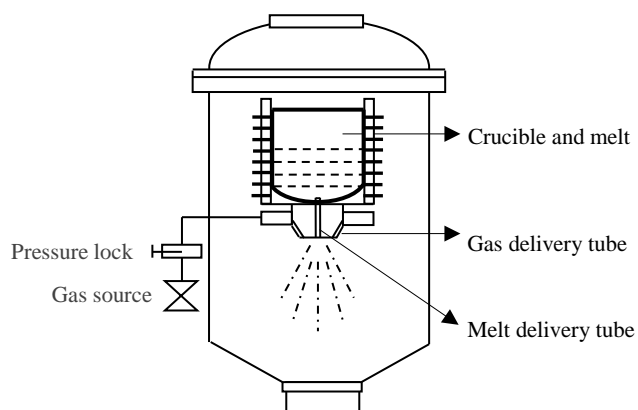


Fig. 1. A schematic diagram of the gas atomizer

A thermometer was immersed in the bottle to monitor the reaction temperature. The second section had a water bath where the gas washing bottle was kept at a constant temperature during the reaction.

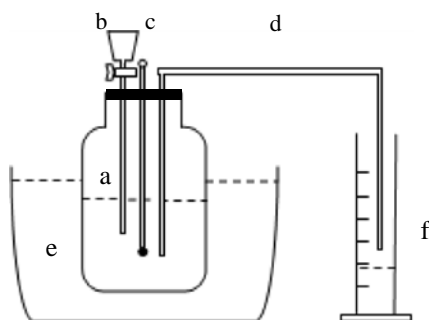


Fig. 2. A diagram of the experimental set up: a – glass reactor; b – funnel; c – thermometer; d – catheter; e – temperature controlled water bath; f – graduated cylinder

Moreover, the third section was a liquid collector which collected the liquid extruded by the H_2 that was produced. Therefore, the volume of the liquid was equal to that of hydrogen. Additionally, ball milling of Mg powder or Mg based material was conducted in a planetary ballmill with stainless steel pots and balls. The ratio of the ball to the mass of powder was 10:1. Moreover, milling was done for 3 h at a speed of 300 rpm and 450 rpm. Milling of half an hour with a 20 minute interruption for heat dissipation. In addition, the phase structure was analysed using an X-ray Diffractometer (XRD, Bruker D8A) with $CuK\alpha$ radiation and scanning speed of $6^\circ/\text{min}$ in 2θ ranging from 25 to 75 degrees. Morphology of the powder was then confirmed through scanning electron microscopy (JSM-7800F, Zeiss Sigma HD).

3. RESULTS AND DISCUSSION

3.1. Phase structure and morphology of gas atomized Mg powders

3.1.1. XRD analysis

Fig. 3 shows the XRD patterns of Mg powders before and after milling. The results show that no other detectable

phases can be found. This indicates that the gas atomization technique is an effective method to produce pure Mg powder.

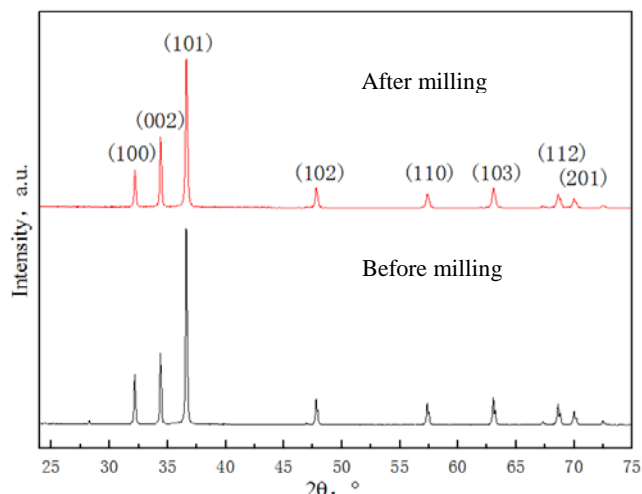


Fig. 3. XRD patterns of atomized Mg powders before and after milling (450 rpm)

In addition, it shows that the velocity of milling is moderate. According to the results, before milling, the FWHM of the top three peaks of the patterns are 0.143, 0.143, 0.156 respectively. After milling, the FWHM turn to 0.174, 0.167, 0.198. Because during ball-milling, the repeated grain breakup, cold welding and re-welding will result in the decrease of crystallite size, which will give a broadening peak in XRD [18–20].

3.1.2. Morphology

The morphology of the powders is significantly affected by ball milling. In addition, most of the gas atomized Mg have an ovoid or nearly spherical appearance and the size ranges between $5\ \mu\text{m}$ and $10\ \mu\text{m}$ (Fig. 4). However, the powders seem an irregular shape after ball milling and the size increased to above $20\ \mu\text{m}$. When ball-milled without any additives for several hours, the powders turn bigger and deformed seriously due to the impacts of ball-to-powder. The increased energy during ball milling deformed the powders and made them to weld together [17, 18].

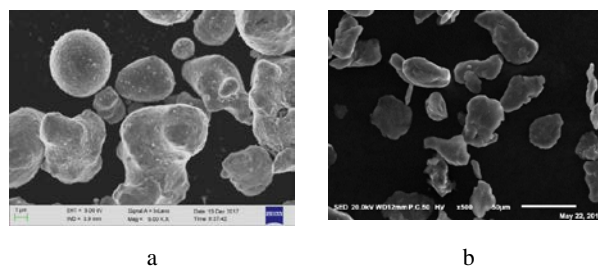


Fig. 4. a – morphology of gas atomized Mg; b – after milling (450 r/m)

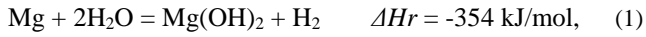
3.2. Reaction for hydrogen generation

3.2.1. Effect of ball milling

The morphology and microstructure of powders are severely destroyed during ball milling, as shown in Fig. 4. Ball milling may also cause other defects, such as a fresh metal surface and new crystal boundaries [19–23]. Notably,

this new surface possesses a high reaction activity which in turn improves the efficiency of reaction with water.

Magnesium can theoretically produce 933 ml/g of H₂ in ambient conditions [19]. The yield curves of hydrogen that was produced by ball-milled Mg powders are shown in Fig. 5. The powder was ball-milled at different speeds at room temperature. In addition, the hydrolysis reaction between the fresh surface of Mg powder and water could be described using the following chemical reaction equation:



Moreover, the reaction process can be divided into three stages, namely; the initial stage, the stable reaction stage and the reaction closing stage (Fig. 5). Without ball milling, the initial stage may last for 10 minutes.

Additionally, the duration of the initial stage may correspond to the time spent on dissolution and breakdown of the passivation layer on the surface of the powders. Therefore, the generation of hydrogen increases slowly and increases significantly when comes to the stable reaction stage.

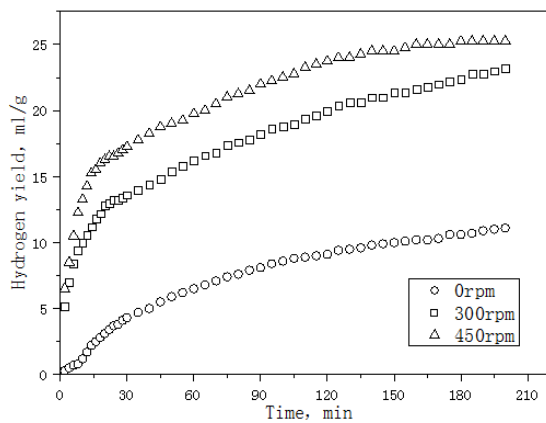


Fig. 5. The yield curves of hydrogen produced by Mg powders ball-milled at different speeds

However, most of the native passivation layer on the surface of the powder was easily broken after ball milling [18]. Moreover, the stable reaction stage occurred at once when the powders came into contact with water and the generation of hydrogen increased significantly. The findings also reveal that the reaction occurs fast at a higher ball-milling speed. For instance, when ball-milling speed is 450 rpm, the hydrogen yield comes to 20 ml/g in an hour, which is more than that at 300 rpm (Fig. 5).

If the reaction proceeds according to Eq. 1, a new passivation layer of Mg(OH)₂ will be produced and it will thicken gradually. This may slow down the reaction and a relatively flat curve will be obtained after 120 min. The percentage of yield of hydrogen can be improved from 1.2 % to 2.7 % by ball-milling, as shown in Fig. 6.

3.2.2. Effect of water temperature

The reaction temperature is always a critical factor in most chemical reactions. In addition, the efficiency of chemical reactions can be improved by elevating the reaction temperature [10]. The present study investigated the production of hydrogen from the reaction between gas atomized high purity Mg powder and pure water at different temperatures. The results in Fig. 7 show that the initial stage

shortens significantly with increasing water temperature. Additionally, the initial stage is the longest (lasts for 10 min) at room temperature (≈ 15 °C).

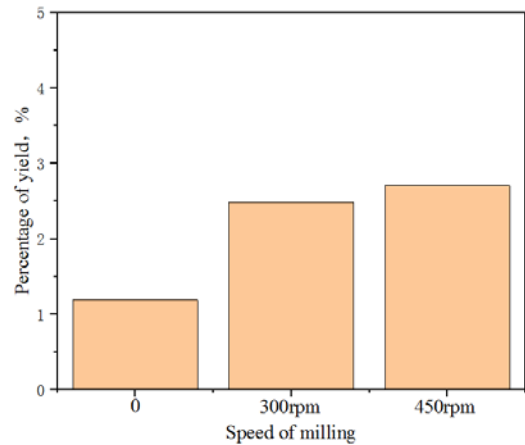


Fig. 6. Percentage of the yield of hydrogen produced by Mg powders that ball-milled

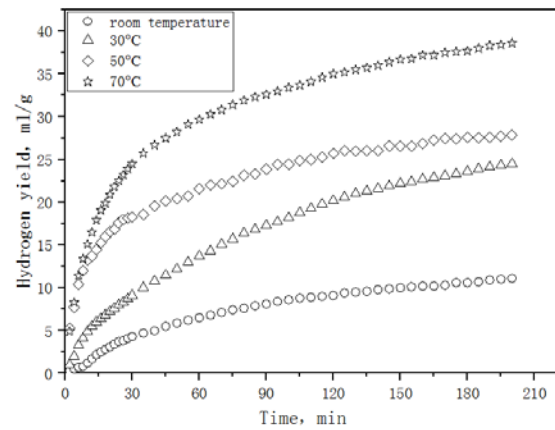


Fig. 7. Hydrogen production curves of Mg powders at different water temperatures

However, the initial stage almost disappears when the temperature of water increases to about 30 °C. Moreover, there was no initial stage when the temperature of water increases to 50 °C and the reaction occurs much faster than in lower temperatures.

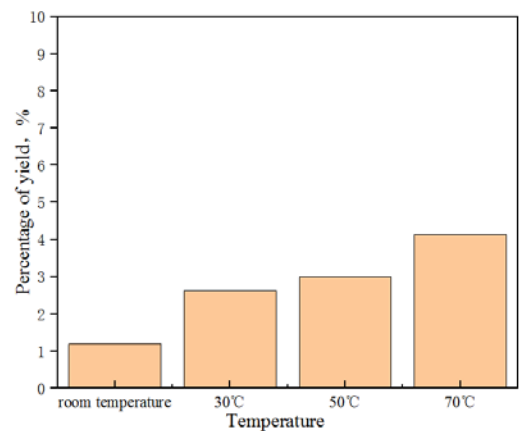


Fig. 8. Percentage of the yield of hydrogen produced by Mg powders under different water temperatures

Generally, the initial stage depends on the rate of the reaction and high temperatures improve this rate.

Furthermore, the solubility of the $\text{Mg}(\text{OH})_2$ layer covering the surface of Mg powder increases in hot water. This further enhances the reaction between the inner fresh Mg powder and water, eventually improving the yield of hydrogen [26]. In addition, high temperature can increase the probability of scouring the $\text{Mg}(\text{OH})_2$ layer on the powders, which also contributes to the thinning and breaking of the layer [14, 16, 17]. The percentage of yield of hydrogen can be improved from 1.2 % to 4.1 % by increasing the water temperature, as shown in Fig. 8.

3.2.3. Effect of ethanol content

Fig. 9 shows the hydrogen production curves of gas atomized high purity Mg powders in different alcoholic solutions at room temperature. Notably, the reaction between Mg and ethanol can be described using the following equation [27, 28]:

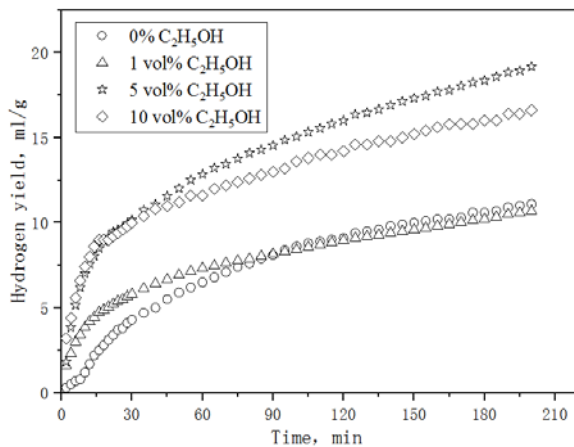
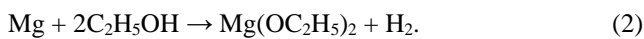


Fig. 9. The hydrogen production curves of Mg powders reacting with different ethanol solutions

As shown in the figure, the maximum yield of hydrogen in an alcoholic solution is about 19 ml/g while that in pure water is only 11 ml/g. This indicates that the reactivity of Mg powder in alcohol is much higher than that in pure water. The difference may be due to the significant passivation of Mg in water, given that $\text{Mg}(\text{OH})_2$ forms more easily than $\text{Mg}(\text{OC}_2\text{H}_5)_2$ [26]. Additionally, the passive $\text{Mg}(\text{OH})_2$ layer on the powder inhibits the alcoholysis reaction [29]. Furthermore, water may modify the pH level of alcohol and this may in turn affect the reactivity of the solution [30]. Therefore, the yield of hydrogen in 5 vol% ethanol solution is far more efficient than that in 1 vol% ethanol solution.

However, when the concentration of the alcohol solution increases to 10 vol%, the total yield of hydrogen will be much less than that in 5 vol%. One major reason behind the unfavorable effect of a high alcohol concentration on the yield of hydrogen is the inductive effect of the alkyl [31]. This results in strong RO-H bonding which lowers the reactivity of the alcohol solution and the effect is more pronounced at a higher concentration of alcohol [32, 33]. Therefore, the yield of hydrogen in a 10 vol% alcohol solution is much lower than that in a 5 vol%. The percentage of yield of hydrogen can be

improved from 1.2 % to 2.1 % by increasing the concentration of the alcohol, as shown in Fig. 10.

3.2.4. Effect of adding NaCl

Fig. 11 shows the yield curves of hydrogen produced from Mg powders that ball milled with different levels of NaCl (wt.%) and reacting with water at 50 °C. The ball milling speed was 300 rpm. The figure shows that the appropriate addition of NaCl may improve the efficiency of hydrogen production. Notably, when the content of NaCl reached 10 %, the yield of hydrogen was nearly 45 ml/g, which was about 40 % more than that obtained from Mg without NaCl.

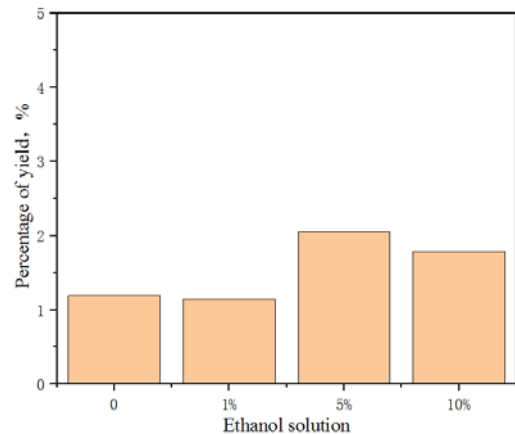


Fig. 10. Percentage of the yield of hydrogen produced by Mg powders reacting with different ethanol solutions

Additionally, increasing the amount of NaCl lead to a significant decrease in the induction period of the reaction, which further improves the rate of hydrogen production. The percentage of yield of hydrogen can be improved from 3.4 % to 4.7 % by milling with NaCl, as shown in Fig. 12.

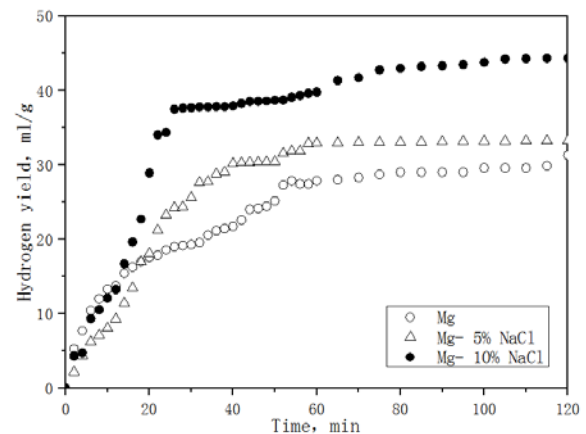


Fig. 11. The yield curves of hydrogen produced from Mg powders that ball milled with different content of NaCl (wt.%)

The benefits of adding NaCl may have been realized in two main ways. First, NaCl is crushed and dispersed during the ball milling process, after which it adheres to the surfaces of Mg powders, as shown in Fig. 13. This may help in preventing the aggregation of Mg powder during ball milling. In addition, the specific surface area of Mg powders will be increased and the reactivity of the reaction is improved. Therefore, high content of NaCl leads to a higher yield of hydrogen [15, 34]. On the other hand, an increase

on the number of Na^+ and Cl^- may improve the conductivity of the solution and enhance the hydrolysis of Mg [16, 35]. Moreover, the increased number of Cl^- may enable them (Cl^-) to replace OH^- of $\text{Mg}(\text{OH})_2$.

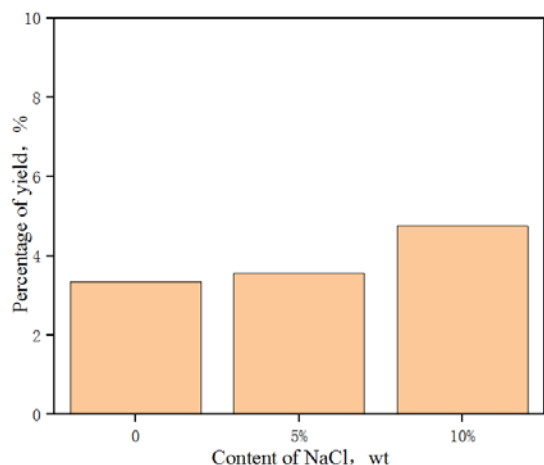


Fig. 12. Percentage of the yield of hydrogen produced by Mg powders that ball milled with different levels of NaCl and reacting with water at 50 °C

This may weaken the $\text{Mg}(\text{OH})_2$ film and promote hydrolysis of the inner metal [36–38]. Therefore, an appropriate increase of NaCl can improve the hydrolysis of Mg powder.

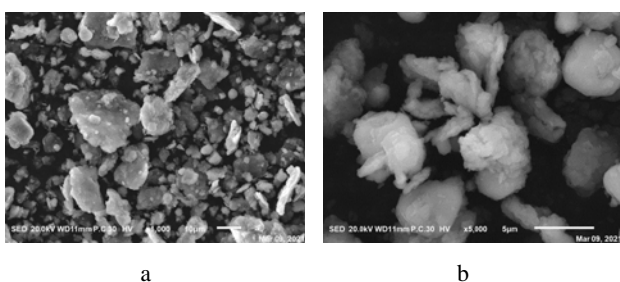


Fig. 13. SEM micrograph of Mg-NaCl (10 wt.%) ball milled for 2 h under 300 rpm: a–1000×magnification; b–5000×magnification

4. CONCLUSIONS

The present study prepared high purity Mg powders at a melting temperature of 990 ± 5 K and atomized pressure of 4.5 MPa. The phase composition and microstructure of the powder were examined through X-ray diffraction and field emission scanning electron microscopy. Moreover, the following conclusions were drawn from studying the hydrolysis reaction with water and alcohol solutions:

1. No impurity phase is introduced into the high purity Mg powders during atomization and ball milling.
2. Ball milling significantly changes the morphology and microstructure of the powders.
3. A higher speed of ball milling improves the hydrolysis reaction given that the yield of hydrogen at a ball speed of 450 rpm is higher than that obtained at 300 rpm.
4. The rate of hydrogen generation largely depends on the temperature of water since a higher water temperature results in a greater hydrogen yield.

5. Moderate amounts of alcohol in water improve the yield of hydrogen although an excessive amount of alcohol may be harmful to the hydrolysis reaction.
6. The yield of hydrogen can be improved by adding NaCl during ball milling and the more the content of NaCl, the higher the hydrogen yield.

Acknowledgments

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