Hydrogen generation from water using Mg nanopowder produced by arc plasma method

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Abstract
We report that hydrogen gas can be easily produced from water at room temperature using a Mg nanopowder (30–1000 nm particles, average diameter 265 nm). The Mg nanopowder was produced by dc arc melting of a Mg ingot in a chamber with mixed-gas atmosphere (20% N₂–80% Ar) at 0.1 MPa using custom-built nanopowder production equipment. The Mg nanopowder was passivated with a gas mixture of 1% O₂ in Ar for 12 h in the final step of the synthesis, after which the nanopowder could be safely handled in ambient air. The nanopowder vigorously reacted with water at room temperature, producing 110 ml of hydrogen gas per 1 g of powder in 600 s. This amount corresponds to 11% of the hydrogen that could be generated by the stoichiometric reaction between Mg and water. Mg(OH)₂ flakes formed on the surface of the Mg particles as a result of this reaction. They easily peeled off, and the generation of hydrogen continued until all the Mg was consumed.

Keywords: magnesium, nanopowder, arc plasma, hydrogen generation, nanopowder production equipment

1. Introduction

Hydrogen gas has long been a promising alternative to fossil fuels. In 2003, the US President George W. Bush announced a proposed budget of US $1.2 billion as part of a hydrogen fuel initiative, with the aim of developing commercial fuel cell vehicles by 2020. Since then, however, interest in the use of hydrogen as a fuel has declined, at the expense of the increased use of biofuels and battery-powered vehicles. Nevertheless, Tollefson [1] reported that ‘hydrogen fuel-cell vehicles, largely forgotten as attention turned to biofuels and batteries, are staging a comeback.’ In other words, the time has come for the use of hydrogen as a fuel to be investigated with renewed interest. Metals that exhibit a strong ionization tendency are considered suitable candidates for hydrogen generation by their reaction with water. The standard electrode potential (E₀/V) of some of the candidate metals decreases in the order Li (−3.03) > K (−2.92) > Ba (−2.90) > Sr (−2.88) > Ca (−2.87) > Na (−2.71) > Mg (−2.69) > Be (−1.85) > Al (−1.66) > Zn (−0.76) (the numerical values represent the standard electrode potentials versus the standard hydrogen electrode, which is set to zero). Metals with a standard electrode potential more negative than that of Mg vigorously react with water to form hydrogen, and reasonable reactivity is expected for Mg, Be, Al and Zn. The authors consider that the rate of this reaction is dependent on the removal of the passivating oxide film from the metal surface.

Deng et al [2–4] succeeded in modifying the surface of Al powder with γ-Al₂O₃ by heating a ball-milled mixture of Al powder (particle size 3 µm) and Al(OH)₃ powder (particle size 2.5–3 µm) in a vacuum at 600 °C for 1h. They found that pure Al powder was relatively inert, but Al covered with γ-Al₂O₃ readily reacted with water, and the amount of generated hydrogen increased with the amount of γ-Al₂O₃. Wang and Chung [5] used oxide nanocrystals such as TiO₂, Co₃O₄, Cr₂O₃, Fe₂O₃ and Mn₃O₄ to modify the surface of Al powder for hydrogen generation in water at room temperature. Gromov et al [6] prepared Al nanopowders...
using electrical explosions of wires and passivated them with Al₂O₃, nickel, fluoropolymer, boron, stearic acid or oleic acid. These passivated Al nanopowders exhibited good stability in 10 wt% NaOH solution. It was found that almost all organic coatings are more efficient than oxides in protecting the Al particle surface against oxidation in water. Astankova et al [7] studied Al nanopowders used in [6] in terms of the kinetics of hydrogen release in 5% aqueous solution of NaOH. The intensity of gas liberation by the Al nanopowders depended on the passivation reagent. The aluminum oleate coating was the most hydrophobic and the Al₂O₃ coating was the most reactive in releasing hydrogen from the aqueous solution. The Al₂O₃-coated Al nanopowder violently reacted to release hydrogen from water at 65 °C and a certain Al/water ratio.

Nakai et al [8] reported hydrogen generation from powder mixtures of CaCO₃ and CaCl₂ with either Al or Mg particles of 60 μm diameter. Ikeda et al [9] found that the raw materials had to be mixed in the optimum proportion for efficient hydrogen generation from mechanically mixed Mg powder (particle size 10 μm) and TiO₂ powder (particle size 0.01–1 μm) or SiO₂ powder (particle size 0.1–10 μm). Grosjean and Rou [10] reported that materials prepared by milling powders of Mg (300 mesh size) and MgH₂ (20 μm) with salts such as KCl, NaCl, LiCl and MgCl₂ generate hydrogen from water.

In the above-mentioned cases, it was necessary to mix a metal oxide or metal chloride with the chief metal to induce hydrogen generation. Meanwhile, Robert [11] reported that by intensive mechanical deformation, pure metal powders can be converted into nanosize crystals and be easily hydrolyzed. Therefore, we consider that hydrogen generation from Al- and Mg-based materials depends on their surface conditions.

Since the 1980s we have synthesized nanopowders of metals [12], alloys [13], nitrides [14, 15], carbides [16] and nanocomposites [17–20] using hydrogen and nitrogen arc plasma. The surface of the metal or alloy nanopowders produced using this method is extremely clean and not oxidized, but such nanopowders burn when exposed to air. This reaction can be prevented by forming a thin oxide layer on the surface of the nanopowder, which we achieved by slowly oxidizing (passivating) the active metal nanopowder in an atmosphere with a low oxygen concentration. For example, Ni nanopowder (average particle size 40 nm) produced by the hydrogen arc plasma method is stabilized [21] by processing for 130–260 min under a partial pressure of atmospheric oxygen of $P_{O_2} = 70–700$ Pa ($P_{O_2} + P_{N_2} = 0.1$ MPa). From the weight increase in the nanopowder due to oxidation, we calculated that the oxide layer that formed on the surface of the stabilized Ni nanopowder was approximately 1 nm thick.

During the course of our study on the reactivity with water of various metal nanopowders (Al, Mg, Zn, Fe, Ni and Ti) subjected to the passivation treatment, we observed the following phenomenon [22]: only the Mg nanopowder vigorously reacted with water to form hydrogen. In this paper, we document this property of Mg and propose the reaction mechanism.

2. Experimental methods

2.1. Preparation of Mg nanopowder

About 7 g of Mg (99.9% purity, 3–10 mm grains, Kojundo Chemical Lab. Co. Ltd) was melted by a dc-arc into a hemispherical Mg ingot in a 5% H₂–Ar atmosphere, which was used as a precursor for the Mg nanopowder. The nanopowder was prepared using a setup built by the authors [23], which was a type of dc arc-melting furnace (figure 1) consisting of (a) a nanopowder generation chamber (arc discharge section) and (b) a nanopowder collection chamber. The material to be converted into a nanopowder is evaporated by dc arc discharge. The evaporation rate increases (decreases) with the increase (decrease) in the partial pressure of the hydrogen or nitrogen gas (normally a mixture of Ar and H₂ or N₂ is admitted to the chamber). The evaporation rate of all metals is higher in hydrogen gas than in vacuum, meaning that a forced evaporation is induced. Since Mg has a higher vapor pressure than other metals, Mg particles are efficiently produced using the forced evaporation method. The production rate of Mg nanopowder is strongly affected by (i) the concentration of H₂ or N₂ in Ar gas at 0.1 MPa pressure and (ii) the electric power (arc current and arc voltage).

In this work, the production rates of the Mg nanopowder were measured as 200 g h⁻¹ at 100 A and 100 g h⁻¹ at 80 A
Figure 2. SEM morphology (a, b) and particle size distribution (c) of Mg nanopowder prepared by the arc plasma method. Most particles are smaller than 500 nm, as shown in (a); however, some particles are as large as 1000 nm, as shown in (b).

at a voltage of 35–50 V in a 100% N\textsubscript{2} atmosphere at 0.1 MPa pressure, that is, 5 kWh of electric power must be applied to nitrogen plasma to obtain 200 g of the Mg nanopowder.

The Mg nanopowder was produced in a 20% N\textsubscript{2}–80% Ar atmosphere at a pressure of 0.1 MPa by applying a dc current of 100 A. It was then stored in a glove box, and the passivation treatment was applied to it at room temperature, before exposing it to air. After passivation, the powder could be handled in ambient air.

The morphology of the particles was observed using a scanning electron microscope (SEM, STEM-5500 Hitachi). The particle size distribution was measured dispersions in ethanol using a particle analysis device (Microtrac DM-S2, Nikkiso Co. Ltd).

2.2. Visual measurement of hydrogen production

The Mg nanopowder was pressed into cylindrical pellets using a hand-driven press. When 20 mg of the Mg pellet (diameter: 3 mm, height: 2.7 mm, porosity: 60%) was added to a sufficient amount of water (200 ml), a reaction started after about 1 min. The amount of released hydrogen gas was measured by the volume of water expelled from an inverted graduated pipette (capacity 10 ml), which was submerged in water. This method was used during the early reaction stage, i.e. from several seconds up to tens of minutes.

The visual observation error was about 0.02 ml. Since the hydrogen generation is given per 1 g of Mg, the visual observation error is about 1 ml.

2.3. Measurement of hydrogen production by gas chromatography

We also evaluated the hydrogen generation by regularly collecting the evolved gas, releasing it into a specific volume of argon and analyzing it by gas chromatography. Equipment used for the study of photocatalysts (detection of hydrogen concentration by water decomposition) was adopted for this measurement. It consisted of a glass reaction container connected to a gas chromatograph. First, 100 mg of Mg nanopowder was placed in the reaction container and about 30 ml of water was poured into the container from the top. This initiated the reaction of Mg with water, releasing hydrogen. In this case, the stoichiometric amount of water necessary for 100 mg of Mg to generate hydrogen is 0.15 ml, but a larger amount (30 ml) was used. The hydrogen concentration was measured by automatically collecting the gas at regular time intervals and analyzing it using the gas chromatograph. Because the minimum collection time was limited to 10 min, this method was adopted for the later stages of the Mg–water reaction.

3. Results and discussion

3.1. Morphology of Mg nanopowder

Figures 2(a) and (b) show SEM images of the Mg nanopowder prepared by the arc plasma method. Most particles are smaller than 500 nm, and one of the largest particles (∼1 µm) is shown in figure 2(b). Figure 2(c) shows the size distribution. It
All Mg particles have the same size of 100, 265 or 381 nm.
The Mg particles are spherical.
There is no interference with the reaction products.

We estimated that the amounts of hydrogen generation rate has a maximum of 0.44 ml s⁻¹ at 150 s then decreases with increasing time.

### 3.2. Hydrogen generation using Mg nanopowder in water at room temperature

We measured how hydrogen generation changed over time when the Mg nanopowder was added to distilled water at room temperature. The nanosize Mg powder floated on the water surface because of the surface tension, thereby hindering hydrogen collection. Therefore, we pressed the Mg nanopowder into cylindrical pellets. In the experiment, we poured 150 ml of distilled water into a 200 ml beaker and added a 20 mg cylindrical pellet. Hydrogen gas bubbles started evolving about 1 min after the Mg pellet was added. The amount of hydrogen (ml) accumulated over time normalized by that for 1 g of Mg is shown in figure 3(a). Figure 3(a) indicates the existence of an incubation time of ∼50 s, after which the amount of generated hydrogen increased rapidly: 22 and 110 ml at 100 and 600 s corresponding to 2.2 and 11% of the Mg nanopowder being consumed in the generation of hydrogen, respectively.

Figure 3(b) shows the increase in the amount of generated hydrogen from 20 min to 40 h. From the gradient of the curves in figures 3(a) and (b), the hydrogen generation rate (ml s⁻¹) was calculated and is plotted in figures 3(c) and (d). The hydrogen generation rate has a maximum of 0.44 ml s⁻¹ at 150 s then decreases with increasing time.

### 3.3. Amount of hydrogen calculated from the thickness of the reaction layer of Mg particles

Figure 3(c) shows that after 150 s the hydrogen generation rate rapidly decreases with time. This reduction can be attributed to the decrease in the surface area of the Mg particles that react with water and to the interference caused by the reaction products. We calculated the amount of generated hydrogen from the weight of the Mg particles that reacted with water under the following assumptions:

1. The Mg particles are spherical.
2. The reaction between the Mg particles and water uniformly proceeds from the surface of the particles to the center. From the thickness of the reaction layer, the mass of reacted Mg can be calculated and converted into the amount of hydrogen. One mole of Mg reacts with two moles of water to produce one mole of hydrogen gas at room temperature (25 °C).
3. All Mg particles have the same size of 100, 265 or 1000 nm.
4. The number of Mg particles (per gram) for each size is the same before and after the reaction.
5. There is no interference with the reaction products.

The amount of hydrogen was calculated as

\[ H_{\text{calc}} = N_0 A (4\pi n^3) (R_0^3 - (R_0 - n)^3) \]

\[ = 7.33 \times 10^{-18} N_0 (3n R_0^3 - 3n^2 R_0 + n^3) \]

where \( H_{\text{calc}} \) is the amount of hydrogen (ml) calculated from the weight of the reaction layer; \( R_0 \) (nm) is the radius of the spherical Mg particles before the reaction with water; \( N_0 \) is the number of particles in a Mg sphere of radius \( R_0 \); \( A = 1005.8 \) ml is the stoichiometric amount of hydrogen released from the reaction between 1 g Mg and excess water at 25 °C and 0.1 MPa; \( n \) is the thickness of the reaction layer (nm); \( \rho = 1.74 \text{g cm}^{-3} \) is the density of Mg.

Figure 4 shows the amount of hydrogen (ml) calculated with equation (1) plotted against the thickness (nm) of the reaction layer on the Mg particles under the above five assumptions for 100, 265 and 1000 nm particles. Both calculated and measured values are given for 265 nm particles. From the data in figure 4 we estimated that the amounts of hydrogen generated by 265 nm particles containing 1- and 5-nm-thick reaction layers are 22.6 and 109.6 ml, respectively. A comparison of these values with the experimental data
revealed that the 265 nm Mg particles released about 110 ml of hydrogen gas in 600 s and that the thickness of the corresponding reaction layer was about 5 nm. As indicated by this example, even a minor change in the thickness of the reaction layer on a nanoparticle may have a pronounced effect on hydrogen generation. While the average size of the Mg nanoparticles was 265 nm, it varied from 30 to 1000 nm. From figure 4 it is clear that even when the reaction layer thickness is constant, the amount of generated hydrogen varies with the particle size. For example, for a reaction layer thickness of 10 nm, the amounts of hydrogen generated from the 100, 265 and 1000 nm particles are 490.8, 210.9 and 59.1 ml, respectively.

3.4. Reaction mechanism of Mg nanopowder with water
We analyzed the Mg nanopowders by x-ray diffraction (XRD) before, during and after the reaction as shown in figures 5(a)–(c), respectively. The pattern in figure 5(a) is dominated by Mg peaks with some contribution from surface

![Figure 3](image_url)

**Figure 3.** Hydrogen generation using Mg nanopowder in water at room temperature: (a) amount of hydrogen (ml) released from 1 g of Mg for times of 0–600 s, (b) amount of hydrogen (ml) released from 1 g of Mg for times of 1.2–144 ks, (c) hydrogen generation rate (ml/s) for times of 0–600 s and (d) hydrogen generation rate (ml s\(^{-1}\)) for times of 1.2–144 ks.

![Figure 4](image_url)

**Figure 4.** Curves showing amount of generated hydrogen (ml) curves calculated from the reaction layer thickness for 1 g of Mg particles with a size of 100, 265 or 1000 nm.

![Figure 5](image_url)

**Figure 5.** Monitoring the Mg-water reaction products by XRD: (a) Mg nanopowder before the reaction, (b) generation of Mg(OH)\(_2\) during the reaction and (c) products after the reaction was completed.
Figure 6. Formation of Mg(OH)$_2$ flakes on Mg nanopowder in water: (a) Mg particle before the reaction, (b) generation of Mg(OH)$_2$ during the reaction and (c) products after the reaction was completed.

MgO produced by the passivation treatment. Figure 5(b) contains signals from Mg, MgO and Mg(OH)$_2$, whereas the pattern in figure 5(c) is dominated by the Mg(OH)$_2$ peaks. Therefore, the reaction of the Mg nanopowder with water can be written as

\[
\text{Mg (solid)} + 2\text{H}_2\text{O (liquid)} = \text{Mg(OH)}_2 \text{ (solid)} + \text{H}_2 \text{ (gas)}.
\]

Equation (2)

Note that our Mg nanoparticles were passivated to enable handling in air by coating them with a 3–4-nm-thick MgO layer. As shown by the experimental results in figures 3(a) and 4(b), the incubation time for the reaction with water was about 1 min; after this incubation time, the reaction progressed rapidly. This experimental finding suggests that a thin MgO layer does not stop the reaction with water.

Hydrogen gas is generated and Mg(OH)$_2$ is produced in accordance with equation (2). Mg(OH)$_2$ has poor solubility in water and forms crystallites from the Mg nanopowder. Phillips et al [25] studied the growth of Mg(OH)$_2$ crystallites and reported that an extremely thin Mg(OH)$_2$ plate (diameter/thickness $= 7.3$) with a hexagonal shape was produced in an aqueous solution with a pH of 10.45. Al-Hazmi et al [26] suggested that Mg(OH)$_2$ nanosheets can be used as an ethanol sensor.

Figures 6(a,a'), (b,b') and (c,c') show SEM images and schematics of a Mg nanoparticle before, during and after the reaction with water, respectively. We selected a large particle with a 1000 nm diameter and observed the evolution of its surface. Figure 6(b) shows the development of Mg(OH)$_2$ flakes during the reaction. These flake-like crystallites are very thin (approximately 5–10 nm) and are oriented normal or parallel to the particle surface. Figure 6(c) shows the final reaction product, which consists of 100% Mg(OH)$_2$ in the form of flakes with the appearance of rose petals. These results reveal that the flake-like Mg(OH)$_2$ crystals generated by the reaction of Mg powder with water do not completely cover the particle surface. Hence the Mg nanoparticle is always in contact with water and reacts with it until it is consumed.

If hydrogen generation proceeds in accordance with equation (2), then the hydrogen storage efficiency of Mg can be estimated to be 8.2 wt%. Much research has been carried out on hydrogen storage materials prepared from Mg or its alloys that absorb hydrogen. At present, hydrogen storage materials are required to store at least 5 wt% hydrogen. MgH$_2$ satisfies this requirement, comprising 7.6 wt% hydrogen. Although Mg cannot react with hydrogen at room temperature to form MgH$_2$, it can do so at high temperatures (above 550 K) and high pressures (above 2 MPa) [27–29]. MgH$_2$ generated under such extreme conditions is reasonably stable at room temperature. This means that heating to 550 K or higher temperatures is required for the desorption of hydrogen from MgH$_2$. Mg-based alloys that absorb and desorb hydrogen at relatively low temperatures are currently being developed. Such alloys include Mg–Fe [30], Mg$_2$Ni [31], Mg$_2$Co [32] and Mg$_2$Cu [33], but they all must be heated to at least 373 K to desorb hydrogen. In addition, their hydrogen storage efficiency (4 wt% or less) is inferior to that of MgH$_2$. In summary, it is difficult to desorb hydrogen from the Mg-based hydrogen storage materials at room temperature.

4. Conclusions

1. We have prepared a Mg nanopowder that vigorously reacts with water at room temperature to generate
hydrogen. For example, when 1 g of the Mg nanopowder (average particle size 265 nm) reacted with water for 600 s, 110 ml of hydrogen gas was generated. This amount corresponds to 11% of the hydrogen that could be generated by the stoichiometric reaction between Mg and water.

2. The hydrogen generation rate of the 265 nm Mg nanoparticles increased with time after the initiation of the reaction, reached a peak at 150 s, and then decreased.

3. The amount of generated hydrogen was calculated assuming spherical Mg particles and various thicknesses of the Mg reaction layer. A comparison of the calculated and experimental values revealed the interdependence of the thickness of the reaction layer and the reaction time. For example, the thickness of the reaction layer after a reaction time of 600 s was 5 nm.

4. To ensure safety when handling the Mg nanopowder in air, it was necessary to form a thin MgO film (with a thickness of approximately 1–5 nm) on the surface of the particles. This was accomplished by storing the particles in an atmosphere of 1% O2 in Ar (0.1 MPa pressure) for about 12 h.

5. SEM images and XRD results indicate that the Mg nanopowder reacted with water and that Mg(OH)2 flakes developed on the surface of the nanoparticles. The flakes detached from the particles, leaving them exposed to water at all times.

6. Using arc plasma discharge, we succeeded in fabricating the Mg nanopowder safely at a high rate of about 200 g h⁻¹ using a low electric power of approximately 5 kW.

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