

## Mg-Ca-Based Hydrolysis Hydrogen Generation Technology

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**Abstract:** Real-time hydrogen generation from hydrolysis of low-cost Mg-based materials is a perfect combination of hydrogen generation, storage and transportation. The theoretical hydrogen storage densities of Mg and MgH<sub>2</sub> are 8.2wt% and 15.2wt% (excluding H<sub>2</sub>O), respectively. However, the main by-product Mg(OH)<sub>2</sub> covers on the surface of the materials during hydrolysis process, thus preventing the reaction from proceeding. We have developed the Mg-Ca-based hydrolysis materials composed of MgH<sub>2</sub> and Ca<sub>4</sub>Mg<sub>3</sub>H<sub>14</sub> phases, which display better hydrolysis performance than pure Mg/MgH<sub>2</sub> because Ca<sub>4</sub>Mg<sub>3</sub>H<sub>14</sub> is prone to hydrolyze, as the byproduct Ca(OH)<sub>2</sub> is more easily soluble than Mg(OH)<sub>2</sub>, providing more gates for water penetration deep into the particles. By adjusting the content of Ca, the mass transfer was enhanced and the conversion rate was improved. By further adding additives (salts, expanded graphite, etc.) and adjusting the reaction solutions (chloride solutions), the pulverization efficiency and hydrolysis performances at low temperatures were improved. Combined with pressing technology, the safety and air stability of the materials were improved. Our work is promising to promote the engineering application of Mg-Ca based hydrolysis materials.

**Keywords:** Mg-Ca alloy hydrides, Hydrolysis, Hydrogen generation

### 1 Introduction

The H<sub>2</sub> generation through the hydrolysis of cost-effective Mg-based materials is a perfect combination of hydrogen generation, storage and transportation, namely “integration of H<sub>2</sub> generation-storage technology”. The theoretical H<sub>2</sub> storage densities of Mg and its hydride (MgH<sub>2</sub>) are 8.2 wt% and 15.2 wt% (excluding H<sub>2</sub>O), respectively.

However, during the hydrolysis process of both Mg and MgH<sub>2</sub>, the main by-product Mg(OH)<sub>2</sub> is produced and deposited on the surfaces of the materials, thereby impeding the progression of the reaction. To break down this barrier, researchers have proposed a series of methods, for example, refining particles to increase active sites, or

breaking Mg(OH)<sub>2</sub> to enhance mass transfer by modifying the materials or adjusting the reaction accelerants[1].

In our work, the Mg-Ca-based hydrolysis materials with better hydrolysis performance than pure Mg/MgH<sub>2</sub> were developed. Mass transfer was enhanced to improve the conversion rate by regulating the content of Ca. By further adding proper additives, the pulverizing efficiency, the hydrolysis performance at low temperature and the air-stability were also improved.

### 2 Experimental procedure

First, the Mg-Ca alloys were prepared in a resistance furnace with high purity Mg (99.9%) and Ca (99.5%) under SF<sub>6</sub>. Then, the Mg-Ca alloys were milled under dry argon atmosphere by SPEX 8000 high energy ball mixer with a ball-to-powder mass ratio of 20:1 for 2 h. Later, the alloys powders were placed in the Sieverts type device and hydrogenated under a hydrogen pressure of 4-5 MPa at 400 °C. It is worth noting that various additives were added during the ball milling process. The generated Mg-Ca-based hydrolysis materials were stored in an argon glove box with <0.01 ppm O<sub>2</sub> and <0.01 ppm H<sub>2</sub>O.

### 3 Result and discussion

#### 3.1 Effect of Ca content on hydrolysis performance

The x wt.% Ca-Mg alloy hydrides (x = 10, 20 and 30) were prepared by hydrogenating the brittle Mg-Ca alloys[2]. The 30 wt.% Ca-Mg alloy hydride (MCH) shows the best hydrolysis properties, which releases 1419.8 mL g<sup>-1</sup> H<sub>2</sub> within 1 h at 70 °C and its conversion rate is about 95%. The superior performances of Mg-Ca alloy hydrides is attributed to an easy hydrolysis nature of Ca<sub>4</sub>Mg<sub>3</sub>H<sub>14</sub> and a high solubility of the by-product Ca(OH)<sub>2</sub>, which provides gates to make water penetrate deeply inside the particles. Increasing the content of Ca enhances the hydrolysis performances of Mg-Ca alloy hydrides due to the formation of more Ca<sub>4</sub>Mg<sub>3</sub>H<sub>14</sub> and larger specific surface areas.

#### 3.2 Common ion effect in the hydrolysis reaction of Mg-Ca alloy hydride-salt composites

The effects of two salts, MgCl<sub>2</sub> and CaCl<sub>2</sub>, on microstructures and the hydrolysis performances of MCH

were investigated[3]. Due to the common ion effect of  $Mg^{2+}$  in the hydrolysis processes, the  $xMCH-MgCl_2$  ( $x = 5, 10, 15$  and  $20$ ) composites generate less  $H_2$  than MCH. The  $10MCH-MgCl_2$  composite milled for 0.5 h displays the lowest  $H_2$  yield of  $962 \text{ mL g}^{-1}$  of the composite at  $25^\circ\text{C}$ , and has slower  $H_2$  generation rate ( $692 \text{ mL g}^{-1}$  in 10 min) than MCH ( $722 \text{ mL g}^{-1}$  in 10 min). At the same conditions, compared with MCH, the  $xMCH-CaCl_2$  ( $x = 5, 10, 15$  and  $20$ ) composites exhibit better  $H_2$  generation performances. Especially,  $15MCH-CaCl_2$  has a  $H_2$  yield of  $1141 \text{ mL g}^{-1}$ .

### 3.3 Low-temperature hydrolysis performances and mechanisms of Mg-Ca-based hydride

The influence of different cations ( $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  and  $NH_4^+$ ) in chloride solutions on low-temperature ( $-20, -10, 0, 10^\circ\text{C}$ ) hydrolysis performances of MCH and mechanisms of interaction are investigated[4]. The results demonstrate that  $Mg^{2+}$  and  $NH_4^+$  in chloride solutions significantly enhance the rate of hydrolysis reaction between MCH and water. In  $NH_4Cl$  solution, MCH exhibits the best initial hydrolysis performance and the highest  $H_2$  yield,  $1198 \text{ mL g}^{-1}$  (MCH) of  $H_2$  is generated within the first 5 min and the final conversion rate reaches 89% at  $0^\circ\text{C}$ . MCH displays the best hydrolysis dynamics in  $MgCl_2$  solution, where the activation energy is low, only  $3.56 \text{ kJ mol}^{-1}$ . This can be attributed to the fact that the types of hydroxide products and the corresponding physical states with respect to the hydrolysis of MCH in various chloride solutions differ with the variations of  $OH^-$  affinity toward  $M^{n+}$  cations (i.e.  $pK/(n+1)$ ) when pH values of chloride solutions are altered. Thus, different low-temperature hydrolysis performances can be observed.

### 3.4 Enhanced air-stability of Mg-Ca hydride-chloride composites

The hydrolysis properties and air-stability of MCH-based material improved by ball-milling with  $NH_4Cl$  are investigated[5]. The addition of  $NH_4Cl$  by ball-milling significantly enhances the hydrolysis performance. The  $MCH-5\%NH_4Cl$  composite (powders) milled for 0.5 h displays the highest  $H_2$  yield of  $1006 \text{ mL g}^{-1}$  at  $25^\circ\text{C}$  without stirring, and has the fastest  $H_2$  generation rate ( $872 \text{ mL g}^{-1} \text{ min}^{-1}$  in the initial 1 min). The air-stability of the MCH-based material significantly increases when being pressed into plate with  $NH_4Cl$  due to the reduction of the contacting areas to the air and hygroscopicity of  $NH_4Cl$ . The  $H_2$  yield of the  $MCH-5\%NH_4Cl$  composite plate still reaches  $726 \text{ mL g}^{-1}$  at  $25^\circ\text{C}$  without stirring

when being exposed to the air for 5 h with 80% humidity at  $30^\circ\text{C}$ .

### 3.5 Hydrogen generation behaviors from hydrolysis of cold-welding free Mg-Ca hydride-expanded graphite composites

The composites including MCH and 0-20 wt% expanded graphite (EG) were explored to examine the impact and underlying mechanisms of EG as additive in mitigating cold-welding and enhancing hydrolysis[6]. EG coats on the material surface as a dispersant to prevent cold-welding, optimize ball milling efficiency and reduce particle size, further facilitating hydrogenation and hydrolysis. In deionized water, MCH with 10 wt% EG (MCH-10EG) displays the best hydrolysis performance, with a low activation energy of  $11.26 \text{ kJ mol}^{-1}$  and a complete conversion within 8 min at  $55^\circ\text{C}$ . Moreover, at room temperature ( $25^\circ\text{C}$ ), combined with the corrosion effects of  $Cl^-$  and  $H^+$  to break the formed  $Mg(OH)_2$  passivation layer, MCH-10EG achieves a complete conversion within only 5 min in  $0.3 \text{ mol L}^{-1} AlCl_3$  solution.

## 4 Conclusion

In our work, the Mg-Ca-based hydrolysis materials composed of  $MgH_2$  and  $Ca_4Mg_3H_{14}$  phases were developed. By adjusting the content of Ca, adding proper additives and adjusting the reaction solutions, the pulverization efficiency, air stability and hydrolysis performances were all improved. Our work is promising to promote the engineering application of Mg-Ca based hydrolysis materials.

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## References

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