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Mg-Mg₂X (X=Cu, Sn) eutectic alloy for the Mg₂X nano-lamellar compounds to catalyze hydrolysis reaction for H_2 generation and the recycling of pure X metals from the reaction wastes



ALLOYS AND COMPOUNDS

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ABSTRACT

The hydrogen generating characteristics of typical Mg-Mg₂X (Cu, Sn) eutectic alloys in the hydrolysis of seawater were investigated. Cu and Sn are cheaper than Nd, Ni, Co, and rare earth elements, and these were used as catalysts in the rapid (30 min) formation of Mg-Mg₂X (Cu, Sn) eutectic alloy in an induction furnace. Hydrogen was evolved in 3.5 wt % NaCl solution (to mimic seawater). Both bulk Mg-Mg₂Cu and Mg-Mg₂Sn eutectic alloys reacted until the Mg ran out. This typical process involves the unique eutectic lamellar structure of multi-layered Mg₂X (as the cathode) stock with Mg (as the anode). This eutectic structure creates numerous nano galvanic-cells in the alloy matrix that accelerates the hydrolysis reaction. The better hydrogen evolution performance was achieved using Mg-Mg₂Cu eutectic alloy because it has the highest electrochemical potential difference (Mg vs. Mg₂Cu:0.32 V > Mg vs. Mg₂Sn:0.17 V). The by-product of hydrolysis was not wasted: an extraction method for recycling the valuable metals (Cu and Sn) at room temperature was developed.

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1. Introduction

Anthropogenic CO_2 emissions are regarded as the leading cause of various phenomena, such as the rapid increase in the mean surface temperature of the earth, rising sea levels, droughts, and food shortages [1,2]. Various innovative technologies for reducing CO_2 emission have been proposed [3–8]. World energy resource surveys [9] show that hydrogen will have an important role in the production of renewable energy. Hydrogen is the most abundant element on earth: it is present in nearly all organic compounds and is naturally abundant in water.

A portable hydrogen generation system can generate hydrogen as an on-demand fuel supplement for vehicle internal combustion engines [10-12], portable electronic devices [12-14] and military applications [15]. The overwhelming majority of industrial hydrogen was obtained by the electrolysis of water or the gaseous reformation of fossil resources. Much effort has been made to develop metal-assisted water-splitting methods to obtain clean hydrogen. Various hydrolysis reactions of metals (such as Mg [16-18] and Al [19]), metal hydrides (such as MgH₂ [20,21] and AlH₃ [22,23]) and borohydrides (such as NaBH₄ [24,25] and NH₃BH₃ [26,27]) with water yield hydrogen. In these water-splitting methods, strong aqueous alkalis were used (Al [28], AlH₃ [23], NaBH₄ [24,25]). According to Jensen [29], alkaline media with high pH (pH 12.9~pH 13.8) can stabilize aqueous sodium borohydride solutions. However, such alkaline aqueous become alkaline wastewater after the hydrogen was generated. In fact, alkaline wastewater is more hazardous than acidic wastewater, because recipient streams were able to attenuate acids than alkalis [30]. The authors of the present investigation previously focused on magnesium-splitting H₂O to form H₂ in neutral chloride solution (simulated seawater) [16,31-41]. Afterward, numerous papers on the magnesium-splitting of H₂O to produce H₂ have been published [39–41]. Producing hydrogen from seawater is attractive because seawater is the most abundant natural resource on the earth. When Mg comes in contact with H₂O, the following reaction occurs.

 $Mg_{(s)} + 2H_2O_{(l)} \rightarrow Mg(OH)_{2(s)} + H_{2(g)} \Delta H_r = -354 \text{ kJ mol}^{-1}$ (1)

According to Eq. (1) [31], the theoretical volume of hydrogen generated by 1 g of Mg is 933 ml at 298 K and 1 atm. In practice,



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however, a protective barrier Mg(OH)₂ grows on the material and covers it, thereby preventing further hydrolysis by Mg [32]. To solve this problem, in our earlier study [32], a platinum-coated titanium net was used as catalyst to speed up the reaction of Eq. (1), and the net was mechanically turned on the bulk Mg surface to remove Mg(OH)₂ layer from the Mg surface. However, the use of an electric motor in a hydrogen-on-demand system is not very practical or energy-efficient. Grosjean et al. [17,18] used high-energy ballmilling to reduce the size of the Mg/Ni powder particles for generating H₂ in neutral water. Zou et al. [42] used cobalt in the ball-milled Mg/Co composite powder to generate H₂ from neutral seawater. However, the ball-milling technique is expensive and consumes a large amount of energy [43,44]. To solve this problem, the present investigation examined the generation of H₂ by splitting water using an Mg-Mg₂X eutectic bulk sample in neutral aqueous NaCl. Herein, the bulk sample reacts with the neutral aqueous NaCl to produce H₂ until all of the bulk becomes reaction waste

In our earlier study [16,32–35], Mg alloy or Mg scrap was remelted and various catalysts (Pt wire, Pt coated Ti net or 304 S.S.) were used to produce hydrogen from seawater. Table 1 presents all the relevant papers on the generation of hydrogen using magnesium alloys in aqueous media. Each paper involves a method of synthesizing Mg alloys for ${\rm H}_2$ generation. Noble metals were commonly used to catalyze hydrolysis using magnesium to generate H₂. As shown in Table 1, the methods for synthesizing Mg alloys in most of the papers [17,18,31,37,38,45] involve ball-milling. The present study and our previous studies from 2005 to 2013 [16,32–36] used melting used melting and casting as an easy way to mass-produce of bulk samples. Recently, Oh et al. [39–41] used melting and casting to produce Mg-2.7 wt.% Ni, Mg-2.7 wt.% Ni-1 wt.% Sn and Mg-3 wt.% Cu alloys for H₂ generation. However, these studies [39–41] did not investigate any process for extracting (or recycling) pure Ni, Cu or Sn from reaction waste [39–41]. Some studies [31,36,38] have made progress in recycling noble metals from the reaction waste after H₂ generation. Our previous study [36] was the first to study the recycling of pure noble metal from the reaction waste after H₂ generation, extracting pure Ni powder from Mg(OH)₂ + Mg₂Ni waste in aqueous NH₄Cl. Huang et al. [31] and Si et al. [38] used aqueous HCl to extract MoS₂ particles [31] and Ag particles [38] from the reaction waste. In the present study, Mg-Mg₂Cu eutectic alloy and Mg-Mg₂Sn eutectic alloy were fabricated for use in the rapidly generating H₂ generation in aqueous NaCl. The activation energies of H₂ generation using the two eutectic alloys were measured. Importantly, a technique for extracting pure Cu and Sn powder from the reaction waste after H₂ generation was developed.

2. Materials and experimental procedures

Pure magnesium, copper and tin ingots were used as starting materials. The Mg-Cu binary system has a binary eutectic point (Mg-Mg₂Cu) at 69.3 wt.% Mg and 30.7 wt.% Cu with a binary eutectic temperature of 485 °C. The Mg-Sn binary system has a binary eutectic point (Mg-Mg₂Sn) at 63.1 wt.% Mg and 36.9 wt.% Sn with a binary eutectic temperature of 561.2 °C. The raw materials for both eutectic alloys were melted in a high-frequency induction furnace at a frequency of up to 35,000 Hz. A mixed gas of 0.5 vol.% of SF₆ in dry air was used as a protective atmosphere, which prevented the molten magnesium alloy from burning. The molten metal was maintained at 700 °C for 30 min until it was homogeneous. Then, the molten alloy was poured into a Y-block permanent mold to solidify. The reduction of water to produce H₂ was performed in aqueous 3.5 wt% NaCl solution with Mg-Mg₂Cu or Mg-Mg₂Sn eutectic compound. In each experiment, the Mg-Mg₂Cu or the Mg-Mg₂Sn sample reacted with 150 ml of the aqueous NaCl. The hydrogen-generating reaction began when the Mg-Mg₂Cu or Mg-Mg₂Sn sample came into contact with aqueous NaCl, and the volume of H₂ that was produced from the samples was determined. The experiments were performed at 5 °C, 25 °C, 45 °C and 65 °C. The hydrogen gas volume was measured five times using the water displacement technique to confirm the experimental data.

Table 1

Literature for H₂ generation from the chemical reaction of Mg alloys in aqueous and the extraction (recycling) of metals from the waste catalysts after the hydrolysis reaction.

Sample	Method	Media for H_2 generation	Extracting (recycling) noble metal from waste catalyst	Reference
Ni-rich AZ91D (catalyzed by Pt wire)	Physical contact	seawater	No	[16] (2005) (the author's previous work)
Mg+10Ni alloy	Ball-milling	1 M KCl	No	[17,18] (2005, 2006)
AZ91D Mg alloy scraps	Melting and cast	5 wt.% NaCl aqueous solution	No	[32] (2007)
(catalyzed by Pt-coated Ti net)				(the author's previous work)
Mg alloy scraps	Melting and cast	3.5 wt.% NaCl aqueous solution	No	[33] (2009) the author's
(catalyzed by Pt-coated Ti net)				previous work)
LGMS plate	Semi-melting and	20 wt.% citric acid + seawater	No	[34] (2009)
	solidification			(the author's previous work)
LGMS plate	Semi-melting and	15 wt.% acetic acid + seawater	No	[35] (2012)
	solidification			(the author's previous work)
Mg-Ni alloy	Melting and cast	3.5 wt.% NaCl	Yes ^a	[36] (2013)
				(the author's previous work)
Mg-Ni alloy	Ball-milling	5 wt.% NaCl aqueous solution	No	[37] (2014)
Mg-Co alloy	Ball-milling	5 wt.% NaCl aqueous solution	No	[37] (2014)
Mg-Cu alloy	Ball-milling	5 wt.% NaCl aqueous solution	No	[37] (2014)
Mg-Ag alloy	Melting and ball-milling	$0.5 \text{ mol } \text{L}^{-1} \text{ MgCl}_2$ solution	Yes ^b	[38] (2014)
Mg-2.7Ni alloy	Melting and solidification	3.5 wt.% NaCl aqueous solution	No	[39] (2016)
Mg-2.7Ni-1Sn alloy	Melting and solidification	3.5 wt.% NaCl aqueous solution	No	[40] (2017)
Mg-3Cu alloy	Melting and solidification	3.5 wt.% NaCl aqueous solution	No	[41] (2018)
Mg-10MoS ₂ alloy	Ball-milling	Seawater	Yes ^c	[31] (2017)
Nd-Ni-Mg alloy	Ball-milling	3.5 wt.% NaCl aqueous solution	No	[43] (2018)
Mg-Mg ₂ Cu eutectic alloy	Melting and cast	3.5 wt.% NaCl aqueous solution	Yes	In this study
Mg-Mg ₂ Sn eutectic alloy	Melting and cast	3.5 wt.% NaCl aqueous solution	Yes	In this study

^a 3 M NH₄Cl aqueous solution, Ni powder.

^b 0.5 mol L⁻¹ HCl, Ag particle.

^c 0.5 M HCl, MoS₂ powder.

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