Journal of Physics: Conference Series

PAPER • OPEN ACCESS

Laser fragmentation of metal powders suspended in water for hydrogen generation

To cite this article: L Escobar Alarcón *et al* 2022 *J. Phys.: Conf. Ser.* **2307** 012010

Laser fragmentation of metal powders suspended in water for hydrogen generation

L Escobar Alarcón[1,*], J L Iturbe García[2], D A Solis Casados[3], S Romero[1] and E Haro Poniatowski[4]

[1] Departamento de Física, Instituto Nacional de Investigaciones Nucleares, Carr. México-Toluca s/n La Marquesa, Ocoyoacac, Edo. de México C.P. 52750, México.
[2] Departamento de Química, Instituto Nacional de Investigaciones Nucleares, Carr. México-Toluca s/n La Marquesa, Ocoyoacac, Edo. de México C.P. 52750, México.
[3] Universidad Autónoma del Estado de México, Facultad de Química, CCIQS UAEM-UNAM, México.
[4] Departamento de Física, Universidad Autónoma Metropolitana Iztapalapa, Apdo. Postal 55-534, CDMX, México.

E-mail: luis.escobar@inin.gob.mx

Abstract. The hydrogen production by laser induced fragmentation of metal powders suspended in water is investigated. Powders of metals such as Al, Mg and three Al-Mg alloys were suspended in distillated water and subjected to laser irradiation to promote a displacement chemical reaction of hydrogen from water. All the studied powders under laser irradiation produced H_2 and the volume rise as a function of the laser fluence, amount of powder and irradiation time following linear behavior. This on-demand production of hydrogen could be an option to release the hydrogen contained in water (H_2O) in situ. Using this configuration, a maximum hydrogen generation rate close to 1.7 mL/min is obtained.

1. Introduction

Hydrogen has been identified as an option for a future energy supply because its advantages as regenerative and environmentally friendly fuel. However, hydrogen in gas form is hardly found on earth and consequently the research of methods to release hydrogen from substances containing hydrogen atoms in their molecules such as water and hydrocarbons is a key issue. Among the different methods proposed, those that do not involve storage and transport of H_2, the main drawbacks of using hydrogen as fuel, are of great interest. An alternative to achieve this on-demand production of hydrogen consists in releasing the hydrogen contained in water (H_2O) because of its abundance and availability. Different methods have been investigated for this purpose such as water electrolysis [1], chemical reactions of hydrides with water [2], water splitting using metal-oxide catalysts [3], and metallic aluminium reacting with aqueous alkaline solutions [4] among others. It is well known that some metals can react spontaneously with water to produce heat and hydrogen gas with the advantage that metals can be used as energy carriers allowing the possibility to generate hydrogen on-demand [5]. It is worth mentioning that as the products of these metal-water reactions are only hydrogen and metal oxides or hydroxides, no carbon dioxide is produced as occurs when hydrocarbons are used making this approach environmentally friendly. Additionally, the metal oxides or hydroxides obtained as byproducts can be transformed again into metals. There are several metals that react spontaneously with water, such as magnesium [6], aluminum [7] and aluminum alloys [8], Fe, Zn, Mn, Zr [5]. Considering their potential energy, storage ability, and low toxicity, a Mg/H_2O or Al/H_2O system would be the first choice. Although Mg/H_2O has lower energy density than the Al/H_2O system, it has a higher reactivity because the aluminum oxide film has good protective properties [9]. However, the main drawback of the aluminum-water or magnesium-water reactions is the formation of an oxide protective layer on the aluminum/magnesium surface, which impedes the contact between the metal and water avoiding the chemical reaction to occur. Different methods to remove the passive alumina layer to favor the aluminum-water reaction have been proposed, however, most of them involve contaminating, toxic, or expensive materials or solutions that must be added to water [10, 11]. Laser radiation has been applied for hydrogen production with interesting results [12-15]; in this line, our research group has reported the generation of hydrogen upon laser irradiation of Al, Mg and three different Al-Mg alloys targets immersed in water with and without the presence of an ultrasonic field [16]; additionally we have proposed an alternative procedure in which laser ablation combined simultaneously with ultrasound was applied to remove the oxide layer of aluminum and/or other metals allowing to induce the chemical reaction with water and consequently releasing high purity hydrogen [17]. In this work a new method to overcome the presence of the native metal oxide layer is reported. This method involves the laser fragmentation of powders submerged in water for hydrogen generation at high rates.

2. Experimental Procedure

The utilized alloys were synthesized by melting following a methodology developed in our Institute (ININ), using a thermal induction oven working at 4.5 kHz and 8 kW in an argon atmosphere. Mg and Al with purity of 99.8% were used as raw materials to prepare three Al-Mg alloys with different Al/Mg ratios, 10/90, 30/70 and 50/50, named Mg10Al, Mg30Al and Mg50Al respectively hereinafter. Powders were obtained by filing pieces of the obtained alloys as well as of pure Al and Mg using a smooth cut file. These powders were placed inside a glass flask, then 20 mL of distillated water were added. The flask was sealed and then connected through a flexible hose to an inverted graduated cylinder filled with water to measure the volume of gas produced by the water displacement method. The powders were dispersed in the water by stirring and afterwards they were irradiated by an unfocused laser beam from a nanosecond Q-Switched Nd: YAG laser emitting at the fundamental line (1064 nm) at 10 Hz. Experiments were performed at room temperature. The effect of laser fluence, amount of powder and irradiation time, on the produced hydrogen volume were investigated. The laser fluence used to irradiate the powder-water mixtures was varied from 0.7 to 1.4 J/cm^2, the amount of powder was changed from 10 to 50 mg using the Mg30Al alloy whereas the irradiation time was varied from 1 to 60 min.

3. Results

The obtained results of hydrogen production, at time intervals of 5 minutes using 20 mg of the different powders irradiated at a laser fluence of 1.2 J/cm^2 are shown in figure 1a). The use of Mg powder produces 7.2 mL of H_2 after 30 minutes of irradiation. When Al is added to Mg in the Mg10Al alloy an important increase in the hydrogen production is observed. In this case 17.5 mL are obtained in 30 min, 2.4 times the obtained with Mg only. The Mg30Al alloy produces the highest amount of H_2, reaching 19.7 mL after 30 min of irradiation at a rate close to 0.65 mL/min. An additional increase in the Al content, alloy Mg50Al, decreases drastically the H_2 production to 6.6 mL which is even lower than the volume produced by the Mg alone. Finally, the lowest H_2 production corresponds to the aluminum powder with a maximum of only 1.4 mL after 30 min. These results show that the powder composition has a crucial effect on the generation of hydrogen.

Because the Mg30Al alloy produced the highest amount of H_2, this sample was used to study the effect of the laser fluence, the amount of powder, as well as the irradiation time on the hydrogen generated volume. Figure 1b) shows that the volume of hydrogen produced after 30 min of irradiation using the Mg30Al alloy increases from 7.5 to 33.9 mL when increasing the laser fluence from 0.7 to 1.4 J/cm^2, with the highest average production rate close to 1.1 mL/min.

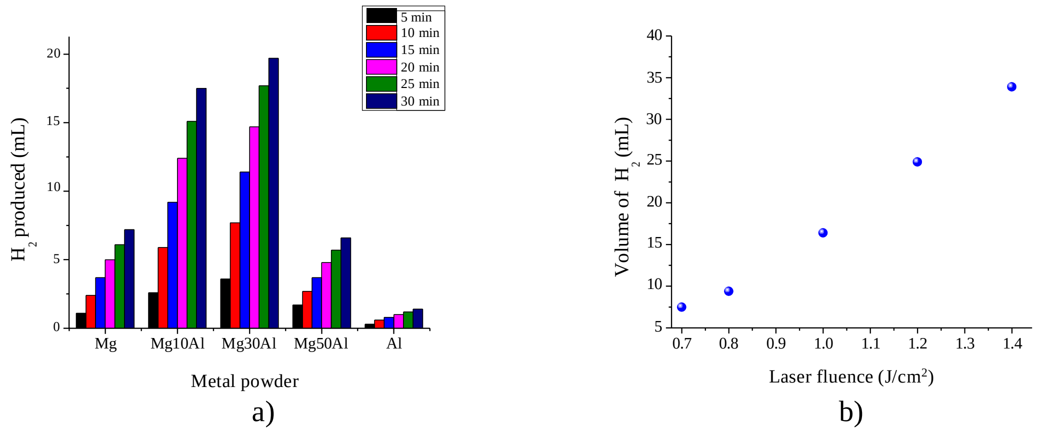

Figure 1. a) H_2 production of the different metal powders after time intervals of 5 minutes of laser irradiation, b) H_2 produced volume as a function of the laser fluence used to irradiate the Mg30Al alloy after 30 minutes of laser irradiation

On the other side, the behavior of the H_2 generated as a function of the irradiation time for the different laser fluences used to irradiate the alloy Mg30Al is shown in figure 2a). In this case the data were acquired every minute. For the fluences used in this work a linear dependence with the irradiation time is observed. The H_2 production rates determined from linear fittings of these graphs are 0.25, 0.32, 0.57, 0.87 and 1.72 mL/min corresponding to the laser fluences of 0.7, 0.8, 1.0, 1.2 and 1.4 J/cm^2 respectively. Concerning the results as a function of the amount of metal powder, it was found that the generation of H_2 increases as the amount of powder increases, from 13.8 mL to 50.4 mL for 10 mg and 50 mg respectively of the Mg30Al alloy. Figure 2b) shows the H_2 produced using the different amounts of powder as a function of the irradiation time. In all cases an almost linear behavior is clearly seen with H_2 production rates of 0.43, 0.68, 0.80, 1.21 and 1.72 mL/min for powder amounts of 10, 20, 30, 40 and 50 mg respectively.

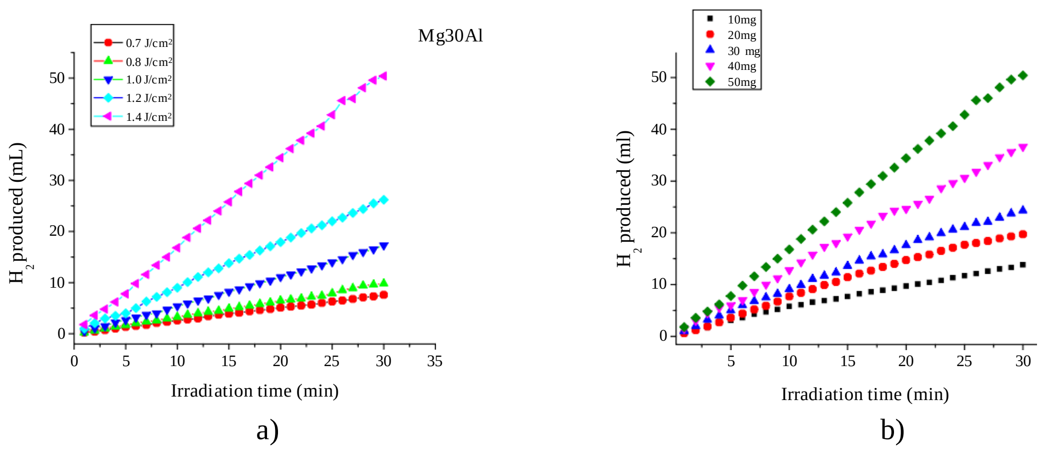

Figure 2. a) H_2 produced volume as a function of the irradiation time for the different laser fluences used to irradiate the Mg30Al powder, b) H_2 produced volume as a function of the irradiation time for different amounts of the Mg30Al powder

In order to determine the temporal limits of the linear behavior, experiments using 50 mg of the Mg30Al alloy irradiated at a laser fluence of 1.4 J/cm^2 were performed extending the irradiation time up to 60 min. Figure 3 shows the obtained results revealing two linear regions in which the H_2 production rate changes drastically; for times lower than 30 min the H_2 production rate is 1.72 mL/min whereas for times higher than 35 min the H_2 production rate is 0.34 mL/min.

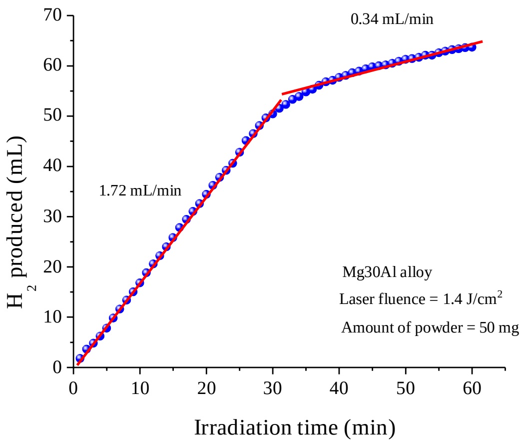

Figure 3. H_2 produced volume as a function of the irradiation time

4. Discussion

The stirring of the metal powders-water mixture does not cause any effect even at times as longer as 60 min. However, when the laser irradiation of suspended powders in water starts two effects are clearly detected, on the one hand the appearance of bubbles on the other hand the sound produced by the interaction laser-suspended particles. A clear increase in the number of bubbles formed when the laser fluence is increased as well as when the amount of powder is greater becomes evident. This can be attributed to the fact that laser irradiation of powders results in the fragmentation of the metal particles, that is, these are divided in smaller parts. It is worth mentioning that the laser-induced fragmentation of nanoparticles (NPs) is a well-known phenomenon that has been investigated for the production of metallic NPs in liquids [18, 19]. In general terms, this process involves the interaction of laser pulses with individual particles suspended in liquid resulting in a decrease in their size with laser exposure time leading to the formation of a colloidal suspension which is clearly seen after a few minutes of irradiation being more evident at higher fluences. As a result of the particle fragmentation new faces, without oxide layer, are exposed in direct contact with water producing the metal-water reaction releasing hydrogen. Figure 4 shows schematically the mechanism proposed for hydrogen generation using this procedure.

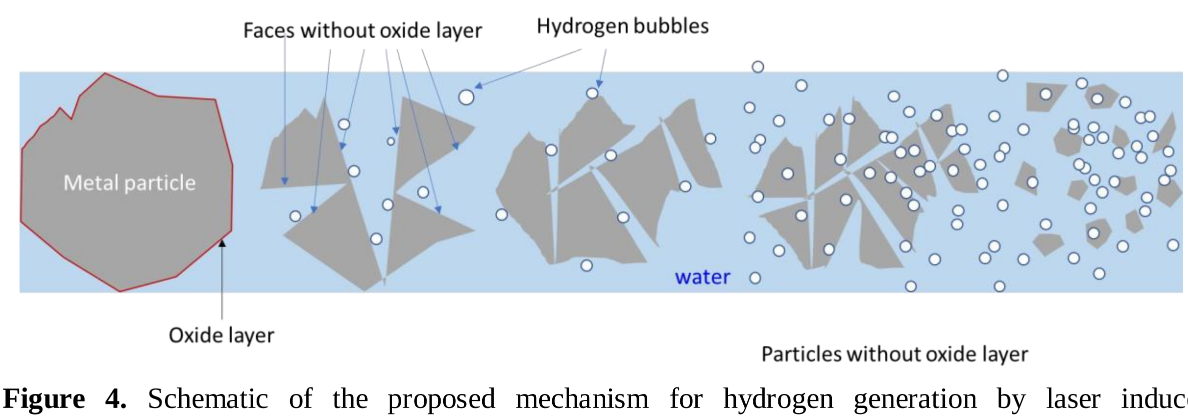

Figure 4. Schematic of the proposed mechanism for hydrogen generation by laser induced fragmentation of metal powders suspended in water

In order to explain the obtained results, as a first approximation at least the influence of the following factors should be considered on the hydrogen production by the proposed procedure: a) the chemical composition of the powders used, b) the laser fluence used to irradiate the mixture powder-water, c) the amount of powder, d) the chemical reactions between the metals and water, and f) the chemical and photochemical reactions between the nanostructures produced and water. Concerning the sound produced by the interaction of laser-suspended particles this can be attributed to the shockwave produced as a result of light absorption by metallic powder particles that originates from their roughness, edges and corners leading to a laser-induced stress wave inside the solid producing an explosive effect with the consequent fragmentation.

One of the best applications for the hydrogen generated using the aluminum-water reaction is in proton exchange membrane fuel cells (PEMFC) to produce electricity being the only byproduct water or water vapor [20]. In order to explore the possibility to use the hydrogen produced by this procedure to generate electricity, a small commercial PEMFC was connected directly to the output of H_2 from the glass flak as is shown schematically in figure 5. The voltage and current produced by the PEMFC were measured showing that immediately after the laser irradiation starts the metal-water reaction begins and induces the hydrogen generation. The voltage delivered by the PEMFC increases rapidly reaching a maximum of 420 mV and a current close to 30 mA, that is, 12.6 mW of electrical power. These results prove that this procedure allows the production of hydrogen of high purity to feed an PEMFC to generate electricity.

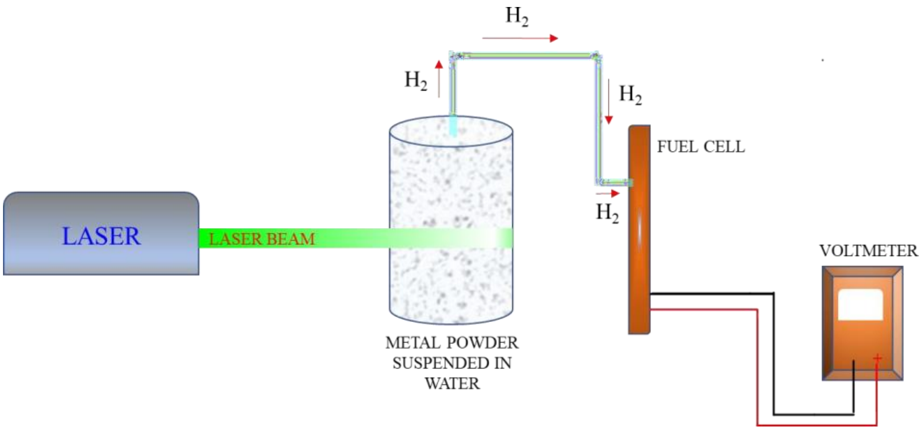

Figure 5. Experimental set up to produce electricity using the hydrogen generated by laser induced fragmentation of metal powders suspended in water

5. Conclusions

A new procedure based on laser fragmentation of metal powders suspended in water for hydrogen production was implemented. This on-demand production of hydrogen could be an option to release the hydrogen contained in water (H_2O). The volume of H_2 generated depends on the powder composition, the laser fluence used to irradiate the powder, as well as the amount of powder used. This configuration allows to obtain a maximum hydrogen generation rate close to 1.7 mL/min. Among the advantages of the proposed procedure the following can be mentioned: firstly, the hydrogen source is water which is abundant on earth, consuming aluminum, magnesium, or their alloys which are cheap raw materials compared to alternative compounds used for hydrogen generation by other methods; secondly the simplicity of the procedure and the very low amounts of material required.

Acknowledgements

This research was partially supported by the CONACYT project CB-240998 and by the ININ Project CB-004. The authors thank Arturo Olalde for his technical assistance.

References

[1] Ursua A, Gandia L M and Sanchis P 2012 *Proceedings of the IEEE*. **100** 410
[2] Wee J H 2006 *J. Power Sources* **161** 1
[3] Kitano M, Tsujimaru K and Anpo M 2008 *Top Catal* **49** 4
[4] Belitskus D 1970 *J Electrochemical Soc* **117**1097
[5] Xu S and Liu J 2019 *Front. Energy* **13** 27
[6] Kravchenko O V, Sevastyanova L G, Urvanov S A and Bulychev B M 2014 *Int J Hydrogen Energy* **39** 5522
[7] Vladimir Shmelev, Vladimir Nikolaev, Ji Hyung Lee and Chungsik Yim 2016 *Int J Hydrogen Energy* **41** 16664
[8] Wang D Y C, Leung M K H and Leung M 2009 *Renewable and Sustainable Energy Reviews* **13** 845
[9] Mei Shuai Zou, Xiao Yan Guo, Hai Tao Huang, Rong Jie Yang and Peng Zhang 2012 *Journal of Power Sources* **219** 60
[10] Porciúncula C B, Marcilio N R, Tessaro I C and Gerchmann M 2012 *Brazilian Journal of Chemical Engineering* **29** 337
[11] Aysel Kanturk Figen, Bilge Coskuner and Sabriye Piskin 2015 *Int J Hydrogen Energy* **40** 7483
[12] Ikuko Akimoto, Kousuke Maeda and Nobuhiko Ozaki 2013 *J Phys Chem C* **117** 18281
[13] Dovletgeldi Seyitliyev, Khomidkhodzha Kholikov, Byron Grant, Omer San and Ali Oguz Er 2017 *Int J Hydrogen Energy* **42** 26277
[14] Shahid M, Bidin N B T and Rehman A 2010 *Optoelectronics and Advanced Materials–Rapid Communications* **4** 1670
[15] Barmina E V, Simakin A V and Shafeev G A 2016 *Chemical Physics Letters* **35** 655
[16] Escobar Alarcón L, Iturbe García J L, González Zavala F, Solis Casados D A, Pérez Hernández R and Haro-Poniatowski E 2019 *Int J Hydrogen Energy* **44** 1579
[17] Escobar Alarcón L, Iturbe García J L, González Zavala F, Solis Casados D A, Pérez Hernández R and Haro Poniatowski E 2019 *Applied Surface Science,* **478** 189
[18] Christian Alexander Schaumberg, Markus Wollgarten and Klaus Rademann 2015 *Phys Chem Chem Phys* **17** 17934
[19] Chubilleau C, Lenoir B, Migot S and Dauscher A 2011 *Journal of Colloid and Interface Science* **357** 13
[20] Shani Elitzur, Valery Rosenband and Alon Gany 2014 *Int J Hydrogen Energy* **39** 6328