Effect of Different Carbon Additives on Hydrogen Storage Properties of AZ31 Magnesium Alloy by High Energy Ball Milling and Equal Channel Angular Pressing

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Abstract. This study investigated the effect of carbon additives on the hydrogen storage performance of AZ31 Magnesium alloy. Different weight percentages (0 wt.%, 3 wt.%) of activated carbon (AC), carbon black (CB) and graphene (G) were used as catalyst to explore the effect of different carbon material additives on the hydrogen storage performance. In addition, the effect of employing different processes like High energy ball milling and Equal channel angular pressing on hydrogen storage performance was also examined. AZ31 magnesium-based composites with different carbon materials were prepared through stir casting method. Micrographs were recorded through OM (optical microscope) and SEM (scanning electron microscope with EDS). The average particle size of the prepared powder samples was measured using particle analyzer. The hydrogenation kinetics was measured using Sievert’s type apparatus. It was found that the addition of carbon materials and refined microstructures effectively enhanced the hydrogen storage performance of AZ31 Mg-alloy. In High energy ball milling process AZ31-3G (graphene) reaches the maximum storing capacity of 6.83±0.04 wt.% within 792±144.34 seconds and desorbed the entire hydrogen in 143 seconds. And in the case of ECAP process, the alloy AZ31-3CB (carbon black) reaches the hydrogen storage capacity of 6.72±0.05 wt.%.

1. Introduction

Based on literature reviews, Magnesium has promising potential capability to store the hydrogen as the chemical metal hydride has higher theoretical capacity (7.6 wt.%). Under certain pressure and temperature, Mg and hydrogen reacts reversibly to form metal hydride and releases the hydrogen. However, the high stability and impoverished hydrogen absorption and desorption kinetics need to be overcome. The properties of hydrogenation can be enhanced by different processing methods and by adding various additive materials[1].

In the field of hydrogen storage, HEBM (High energy ball milling) is one of the most common methods to prepare storage alloy powders. High energy ball milling process improves the hydrogen storage performance thereby possessing reduced particle size. E. David et al.[2] used the HEBM process to prepare Mg powder and the observed results shows that the rate of hydrogen absorption and desorption...
was effectively increased. The reason is that after the ball milling process, large amount of defects was produced, which in turn causes the reduced particle size, and increased surface area. The ball milled MgH₂ released the hydrogen after about 12 minutes. Andresen et al. [3] also used HEBM process to prepare magnesium-aluminum alloys as hydrogen storage materials and the kinetic properties were studied. It was found that the presence of Al in the materials can increase the dissociation rate of hydrogen molecules into the materials and greatly enhance the hydrogen release at constant rate. Later on, Z. Lan et al.[4] improved the hydrogen storage performance of Mg-Al-Li solid solution by sintering, annealing and HEBM process. The hydrogenation properties with respect to the effect of different preparation methods were studied and the results were also studied elaborately. The solid solution which is milled for 70h reached the maximum storage capacity of 3.7 wt.% in 80 mins. In 2009 J. C. Crivello et al. [5] prepared the Mg-Al alloy powders through high energy ball milling process in the presence of Nb₂O₅ as catalyst for hydrogen storage. Materials such as Mg, Mg₁₇Al₁₂ and Mg₂Al₃ alloy powders reaches the weight capacity of 4.7 wt.% at 250°C with reproducible conditions. Graetz J et al [6] found that the aluminum metal hydrides, could release the hydrogen gas at 170°C which is far lower than the hydrogen release temperature of Mg metal hydride at 300°C. The decomposition of aluminum metal hydride(AlH₃) is only 10KJ/mol, hence it was understood that the addition of Al metal as an additive, reduces the thermodynamic stability of Mg-based hydrogen storage materials. Thus the ball milling process significantly improve the hydrogenation properties.

Just like ball milling process, ECAP is also another common economical method for preparing high-performance materials by applying shear stress deformations. Jacques Huot et al. [7] reviewed the ECAP technique for AZ31-Mg alloy at four different temperatures of 250° C, 200 ° C, 250° C and 300 ° C respectively with two passes of B₄ route. The analysis illustrates that the recrystallization phenomenon occurs at an elevated temperature level. In the higher extrusion temperature, it is easier to successfully carry out the ECAP process which significantly affects the grain refinement and enhances the kinetics through nucleation. Krystian M et al.[8] improved the hydrogenation kinetics for the Mg alloy Zk60 by using plastic deformation process. The effect of grain size and the catalyst on hydrogenation absorption and desorption rate were discussed. The material which has the smallest grain size desorb the maximum capacity of 6.6 Wt.% in less than 5 mins. N. Skryabin et al.[9] processed the pure Mg, Zk60, and AZ31 magnesium alloys through the ECAP, and the observed results shows that the kinetics of hydrogen absorption and desorption was enhanced four times faster, after the deformation process. In addition, the thermal characterizations were also examined for MgH₂. The Experimental results revealed that ECAP decreases the activation energy of MgH₂.

The another most effective tactics to improve thermodynamic properties and kinetics is adding the carbon-based materials to the Mg alloy powders because of its novel electro nature. Wu C.Z et al.[10] reported the advantages of various carbon additive materials such that single wall Nano carbon tube (SWNTs), fullerene, carbon black (CB), activated carbon (AC), and asbestos to improve the hydrogen storing capacity. Simultaneously in developing de-/hydrogenation kinetics of magnesium, the carbon additive materials exhibit the benefits significantly and reaches the capacity of 6.2 wt.% in 10 mins.

The above literatures reveal the significance of using catalysts and different processing methods for enhancing the hydrogen storing capacity. In the present work, the composites were prepared through the gravity casting method. And this work also illustrates the combined effects of different process (plastic deformation and milling) with three different types of carbon additives such as activated carbon (AC), carbon black (CB) and graphene (G) on the hydrogen absorption and desorption kinetics properties to the magnesium alloy based storage materials.

2. Experimental methods

2.1 Experimental materials.
The substrate materials used for the experiment was AZ31-Mg alloy purchased from Xiangguang Co., Ltd. The carbonaceous additives such as activated carbon (AC), carbon black (CB), and graphene were purchased from First Chemical Co., Ltd. and Anju Technology Co., Ltd. The composition of the additive carbon materials to the Mg alloy were shown in Table 1.

| Simplified name | Experimental material name |
|-----------------|----------------------------|
| AZ31-0 C (Pure AZ31) | 0wt.% C (carbon)-AZ31 magnesium matrix composite |
| AZ31-3AC | 3wt.% AC (activated carbon)-AZ31 magnesium matrix composite |
| AZ31-3CB | 3wt.% CB (carbon black)-AZ31 magnesium matrix composite |
| AZ31-3G | 3wt.% G (graphene)-AZ31 magnesium matrix composite |

2.2 Experimental Equipments

AZ31/C (C- carbon materials) composites were prepared through the resistance heating furnace, and molten metals are allowed to flow into the mold for solidification by the gravity stir casting method. During the casting process, the entire system was prevented by argon gas from the phenomenon of oxidative burning [11]. Then the sliced dimension of 11.5 × 11.5 × 75 mm was treated with the homogenization heat treatment at 400 °C for 24 hours and then suddenly it was quenched with water. It was found that quenching technique affects the microstructures and increases the ductility of the materials. The billets were deformed through ECAP according to Bc route (90° rotations among each pass) with 8 passes at 300°C. A die angle of 120° was used to deform the materials billet and finally the powders were comminuted through rasp filling for hydrogenation. Finally, the obtained powders from manual rasping were processed by ball milling. The experiment was carried out in Retsch PM100 planetary ball mill with a ratio of the ball to powder as 30:1 and the revolution speed was maintained at 300 rpm for 4 hours. The distribution of particle size was also measured before the hydrogenation process. Micrographs of the samples were recorded by optical microscopy (OM) and the morphologies of the powder samples were observed via (SEM) scanning electron microscope of model no. (JSM-6390LV) with EDS analysis. To measure the interaction between alloy and hydrogen gas, a closed volume system manipulated by LABVIEW software was used. 0.1 g of sample was placed inside the reactor at a temperature of 375°C with the absorption and desorption pressure of 35 atm and 8 atm respectively. Hydrogenation characterizations were analyzed through Sievert’s measurement system.

3. Results and discussion.

3.1 Micrograph analysis.

The optical microscopy observations of pure AZ31 alloy material was shown in Figure 1. The grain refinement of the alloy after deformation was also investigated. It was observed that the grain of AZ31 magnesium alloy was significantly smaller after ECAP process (Figure 1 (c)). Hence it was proved that ECAP method was effectively refining the grains via plastic deformation [12].
The grain sizes of the deformed materials after 8 passes are evaluated and the observed sizes were presented in Table 2. Among the three type of carbon material additives, the grain size obtained by the addition of carbon black (CB) after ECAP method has the smallest grain size. The reason speculated that the average particle size of the carbon black at about 30nm causes more nucleation sites during the melting process which results in the lowest grain size. In the case of activated carbon, the particle size at about 20 μm was supposed to form slight bigger grains. The grain size observed after graphene additions was largest among others. The agglomeration of graphene results in the uneven distribution of grains during melt casting because of its low density (0.027 g/cm³). And it was also found that the grain refinement effect is obliviously less in ECAP process. The EDS analysis of the prepared AZ31-3G sample was shown in Figure 2. EDS analysis shows that the prepared AZ31-3G sample contains large amount of carbon content. In addition, the presence of oxygen element was attributed due to the formation of an oxide layer over Mg alloy on exposure to open atmosphere. Therefore, for hydrogenation experiments the samples were prepared an hour prior, to prevent the oxide formation.

Table 2. Grain size after 8 passes of ECAP process.

| Sample type | AZ31-3AC | AZ31-3CB | AZ31-3G |
|-------------|----------|----------|---------|
| Grain size (μm)  | 7.07     | 4.35     | 14.14   |

3.2 Particle size analysis.
AZ31 Mg-alloy with different carbon materials powder particles were refined by HEBM technique. The particle size of the metal powders was analyzed through laser particle size analyzer and the observed values are given in Table 3. The AZ31 with carbon composites contain the smaller particle size than the pure AZ31. Among them, AZ31-3G has the best refining effect with lowest particle size. The lesser specific density of graphene (G) has the largest volume, which greatly increases the collision area in HEBM process. Similarly, the carbon black (CB)has the smaller particle size than activated carbon (AC). The results exemplify that addition of carbon materials could effectively improve the metal powder particle refinement in the milling procedure.
Table 3 Particle size of powders after HEBM process.

| Sample     | Average particle size (µm) | Particle size distribution (µm) |
|------------|-----------------------------|---------------------------------|
|            |                             | d (0.1) | d (0.5) | d (0.9) |
| AZ31       | 74.74                       | 28.98    | 62.95   | 128.5   |
| AZ31-3AC   | 64.53                       | 24.26    | 52.27   | 116.98  |
| AZ31-3CB   | 42.35                       | 14.84    | 23.33   | 71.48   |
| AZ31-3G    | 39.18                       | 17.22    | 34.55   | 66.4    |

3.3 Hydrogen absorption and desorption characteristics.
The prepared sample powder was subjected to hydrogenation measurement after the activation treatment. Average of five hydrogen absorption and desorption cycles were compared. Figure 3 (a, b) explains the kinetic curve of different carbon additives to the AZ31 alloy which is processed by ECAP process. Results explain that activated carbon and carbon black with AZ31 effectively enhances the kinetics of hydrogenation. The material with 3 wt.% of carbon black (CB) has excellent hydrogen storage performance which reaches the maximum capacity of 6.72±0.05 wt.% see Table 4. The deformed material which has the smallest grain size contain the better kinetics in hydrogenation [8]. Moreover, the graphene added material was fractured easily during deformation which causes the poor grain refining effect that in turn decreases the hydrogenation performance. Figure 3 (c, d) shows the sorption rate of various composites by HEBM method. The material milled with 3 wt.% graphene (G) absorb and release the H₂ gas faster with maximum storage capacity of 6.83±0.04 wt.% as presented in Table 4. Material which has the lowest particle size in ball milling causes the higher surface area which increases the rate of hydrogenation. In addition, the graphene crystalline structure possesses the catalytic effect on MgH₂ decomposition facilitating the reaction [13].

Fig 3. Hydrogen absorption and desorption curve (a). Absorption-ECAP, (b) Desorption-ECAP, (c) absorption-HEBM, (d) desorption-HEBM.
Table 4. Average Hydrogen kinetic rate and capacity for various compositions.

| Sample   | Process | Absorption time (s) | Desorption time (s) | Absorption capacity (wt.%) | Desorption capacity (wt.%) |
|----------|---------|---------------------|---------------------|-----------------------------|-----------------------------|
| AZ31     | ECAP    | 1968±196.01         | 266.8±36.06         | 6.51±0.04                   | 6.51±0.04                   |
|          | HEBM    | 2024±274.34         | 239.6±44.05         | 6.41±0.05                   | 6.41±0.05                   |
| AZ31-3AC | ECAP    | 1872±190.01         | 248.8±19.07         | 6.61±0.04                   | 6.61±0.04                   |
|          | HEBM    | 1660±156.01         | 223.2±47.03         | 6.72±0.07                   | 6.72±0.07                   |
| AZ31-3CB | ECAP    | 1567±174.34         | 229.6±31.06         | 6.77±0.05                   | 6.77±0.05                   |
|          | HEBM    | 1244±189.34         | 193.6±17.03         | 6.79±0.04                   | 6.79±0.04                   |
| AZ31-3G  | ECAP    | 2171±254.67         | 293.2±33.07         | 6.21±0.06                   | 6.21±0.06                   |
|          | HEBM    | 792±144.34          | 143.2±26.09         | 6.83±0.04                   | 6.83±0.04                   |

4. Conclusions.
This study reveals the comparative effects of carbonaceous addition and different process (ECAP and HEBM) on hydrogenation properties of AZ31-Mg alloys. The composite alloy materials were prepared through gravity stir casting technique. Activated carbon and carbon black addition to the AZ31 alloy has better grain refinement in the Equal Channel Angular pressing process. The material with smaller grain size have more boundaries to diffuse the hydrogen inside the materials thus the AZ31-3 CB (carbon black) can effectively absorb the hydrogen of 6.72±0.05 wt.% in 1567±174.34 seconds and desorbed it in 229.6±31.06 seconds. Similarly, in the case of high energy ball milling, the large surface area produced by the small particle size for the alloy AZ31-G (graphene) shows the better kinetics among all the prepared materials which reaches the maximum capacity of 6.83±0.04 wt.% within 792±144.34 seconds and release the entire content in 143±26.09 seconds. From the commercial point of view, the energy consumption of HEBM is higher than the ECAP process, and the powder samples need to be stored in a special environment (vacuum, inert gas, etc.) to avoid the oxidation process. Therefore, in conclusion, the ECAP technique is more economic for hydrogenation than the HEBM with better kinetics results.

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