A Comparative Analysis of Hydrogen Storage Characteristics in AZ31 Magnesium Alloy with the Addition of Graphene and Carbon Nanotubes via Ball Milling Process

Song-Jeng Huang*, Wei-Da Lin and Veeramanikandan Rajagopal

Department of Mechanical Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan

Abstract: In the present investigation, an examination was conducted on the hydrogen storage performance of industrial waste grade AZ31 magnesium alloy when combined with either Carbon Nanotubes or Graphene. This study aims to understand the enhancement of hydrogen storage properties reinforced with polymer materials, such as Graphene or Carbon Nanotubes. The experimental samples, composed of AZ31 Magnesium Alloy combined with either Carbon Nanotubes or Graphene, were crafted through gravity casting. Thereafter, a high-energy ball milling process was employed to further refine the hydrogen storage material powders. The micrographic structures of all the sample powders were analyzed by x-ray diffraction (XRD), and scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS). Additionally, the average particle size distributions of the sample powders were quantified for comprehensive characterization. The absorbed and desorbed hydrogen capacity and kinetics was calculated by a Sievert's type apparatus. Overall, the performance of the sample powder AZ31-0.1G showed the highest absorption and desorption at a rate of 0.0036 wt%/s and 0.0084 wt%/s. Moreover, the hydrogen capacity of AZ31-0.1G reached the highest value at 5.32 wt%. The acquired data unveils that with the adding of either Graphene or Carbon Nanotubes as additives significantly improved the hydrogen storage capacity of AZ31 magnesium alloy.

Keywords: AZ31 magnesium alloy, Carbon Nanotubes, Graphene, high-energy ball milling, hydrogen storage.

1. INTRODUCTION

In the present era, the world is facing increasingly severe environmental challenges, resulting in global warming, climate change, pollution, and environmental degradation. This has prompted researchers worldwide to focus on developing cleaner and greener energy technologies. Hydrogen, given its non-harmful characteristics, is considered a highly dependable option for substitution in place of traditional fossil fuels [1-4].

Magnesium alloys stand out for their remarkable combination of low density and robust mechanical properties, making them an exemplary choice for various applications. Additionally, their exceptional performance in secondary processes further enhances their versatility [5]. Moreover, these materials excel in area of hydrogen storage, underscoring their commendable attributes in advancing technological and industrial capabilities, showing a promise for use in mobile transport applications, thanks to their high storage capacity and safety features [6]. There have been significant endeavors to enhance solid-state systems for hydrogen storage, particularly focusing on metal hydrides [7]. Among these, magnesium hydrides (MgH_2) have shown a significant performance due to their favorable hydrogen storage property, including good potential of hydrogen storage capacity (7.6 wt%) [8]. Nevertheless, the slow hydrogen absorption and desorption performance pose a primary constraint for magnesium-based alloys in the field of hydrogen storage [9]. Consequently, various processing techniques have been employed to enhance the hydrogen storage properties of the materials [10].

A effective method to process hydrogen storage materials is through high-energy ball milling, A research study by Veeramanikandan Rajagopal *et al*. Prepared hydrogen storage powders for AZ31 and AZ91 magnesium alloys using a high-energy ball milling process. The enhancement of hydrogen storage properties was achieved through the generation of a substantial number of defects, resulting from a reduction in particle size that leads to an increase of surface area [11].

Exploring the improvement of MgH_2 properties through elemental reinforcements, microstructure adjustments, and compositional changes. Multiple experiments have demonstrated the considerable effectiveness of incorporating carbonaceous additives [13]. Therefore, the study for acknowledging the effect of magnesium-based alloys reinforced with carbonaceous additives is essential. A research study by Aqeel Abbas al et. Conducting a hydrogen storage test using ZK60 magnesium alloy that underwent equal-channel angular extrusion and high-energy ball

*Address corresponding to this author at the Department of Mechanical Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan; E-mail: sgjghuang@mail.ntust.edu.tw

milling. The alloy was augmented with 5 wt% of carbon nanotubes (CNTs) and 5 wt% of graphene for the experiments [14]. On top of that, A research study by Song-Jeng Huang al et. Comparing the hydrogen storage properties of AZ31 magnesium-based alloy reinforced with various of carbonaceous additives processed through ECAP and HEBM [15, 18], contributing precious expertise to enhance the hydrogen storage properties of magnesium-based alloy. Broader research underscores the potential of carbonaceous additives in enhancing hydrogen storage, these materials offer unique properties, like high surface area and porous nature which address critical storage challenges [16, 17].

In the course of this study, we focused on the synthesis of hydrogen storage composite materials involving AZ31, combined with either carbon nanotubes or graphene, utilizing the gravity casting method. To refine the particle size of the resulting samples, a high-energy ball milling process was applied. This refinement process confers several key advantages to the sample powder, playing a pivotal role in enhancing hydrogen storage properties. The advantages include an augmented surface area, improved kinetics, optimal thermodynamics, reduced diffusion path lengths. These significantly contribute to achieve superior hydrogen storage properties.

The impact of carbonaceous additives on hydrogen storage properties and the composition of the microstructure during dehydrogenation/hydrogenation kinetics was thoroughly examined and compared for discussion.

2. EXPERIMENTAL

2.1. Material

The carbon nanotube, with an average diameter of 9.5 nm, is sourced from Top Nano Technology Co., Ltd., while the graphene, with an average diameter of 5 nm, is supplied by Enerage Inc. In the course of our comprehensive study, we engineered commercial Mg-based alloys of AZ-series material, specifically focusing on the AZ31 Magnesium Alloy (comprising 3.08% Al, 0.908% Zn, 0.393% Mn, and the balance being Mg) [11]. This alloy, crucial to our research, was procured from the esteemed Kuangyue Co., Ltd.

2.2. Experimental Procedure and Method

The gravity casting technique is employed to fabricate the present of Mg ingot. The experimental setup of the furnace is illustrated in Figure **1**. In this study, AZ31 magnesium alloy was chosen as the substrate, and nano carbon tubes (CNTs) and graphene were incorporated as composite reinforcement elements at ratios of 0 wt%, 0.1 wt%, and 0.2 wt%. The preparation involved gravity casting combined with mechanical stirring to produce ingots. The fusion process took place within a resistance melting furnace, where both the base material and reinforcing components were placed. The temperature

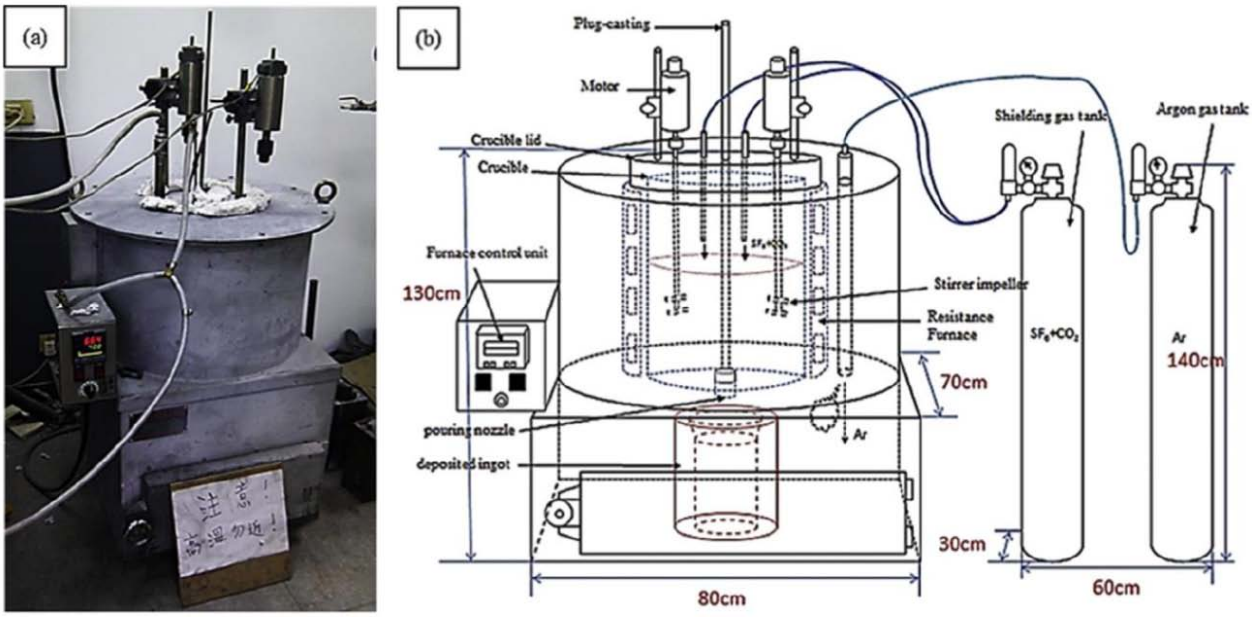


Figure 1: (**a**) Experimental setup of the furnace used for the fabrication of the Mg ingot; (**b**) Schematic rendering of the furnace [12].

was elevated to 400 °C, and SF6 gas was introduced, succeeded by the introduction of argon gas at 600°C to safeguard the molten metal. Stirring ensued for 20 minutes at 750 °C to achieve a uniform dispersion of the reinforcing material. Following a brief 10-minute interval, the molten material was poured into molds, left to cool naturally, thereby concluding the casting procedure.

Following this, the powder samples were readied for the hydrogenation reaction through the manual dispensing of 3 g of alloy powder from each sample for high-energy ball milling (HEBM). Before initiating the hydrogen reaction, the test samples underwent mechanical grinding in an alloy mill for 4 hours within an inert atmosphere, maintaining a powder-to-ball weight ratio of 1:30. The rotation speed was set at 300 rpm. All measurements and transmission tests for the samples were conducted under glove box protection, utilizing highly pure argon gas.

An scanning electron microscope (SEM) apparatus was utilized to analyze surface morphologies of the samples, and energy dispersive spectroscopy (EDS) was employed for further elemental identification. The examination of phase transformations in the alloy powders was conducted through

x-ray diffractometer (XRD), utilizing a Cu-Ka ray source in the range from 20° to 80°, with a step of 0.05°/0.5 s [15]. To assess the interaction with hydrogen gas, activation occurred in a closed volume Sieverts-type system for 60 minutes at a temperature of 375°C. Hydrogen reaction kinetics were subsequently measured under a hydrogen absorption and desorption pressure of 35 atm.

3. RESULT AND DISCUSSION

3.1. Material Characteristics

The SEM images and EDS elemental maps, illustrated in Figure **2a-e**, for the AZ31 magnesium alloy processed through HEBM reveal the formation of Magnesium and Aluminum. Additionally, the absence of the Zinc and Manganese element is observed on the surface. Despite their low concentration in the AZ31 alloy, both Manganese and Zinc can be acted as catalysts [15]. The high-energy ball milling process effectively reduces particle size and enhances the specific surface area of the tested alloys. The reduction in particle size and the subsequent increase in surface area contribute to enhancing the reaction surface area between the powder and hydrogen. This, in turn, further improves the hydrogen absorption and desorption kinetics of the powder.

3.2. Material Particle Size

AZ31 magnesium alloy particles without carbon additives exhibited a larger size. In contrast, among the carbon additives, the AZ31 alloy with added graphene or CNTs (AZ31-0.1G, AZ31-0.2CNTs) demonstrated more pronounced refining effects as shown in Figure **3**.

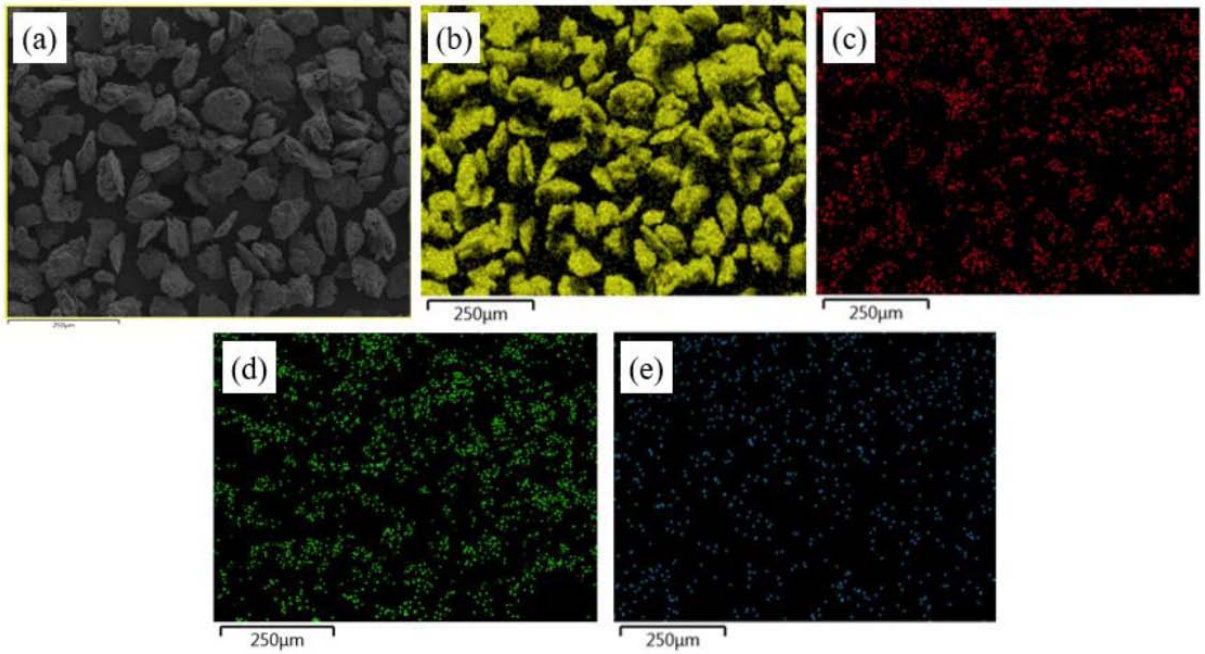


Figure 2: SEM images of (**a**) Pure AZ31 and elemental maps of (**b**) Mg (**c**) Al (**d**) Zn (**e**) Mn after HEBM-processed.

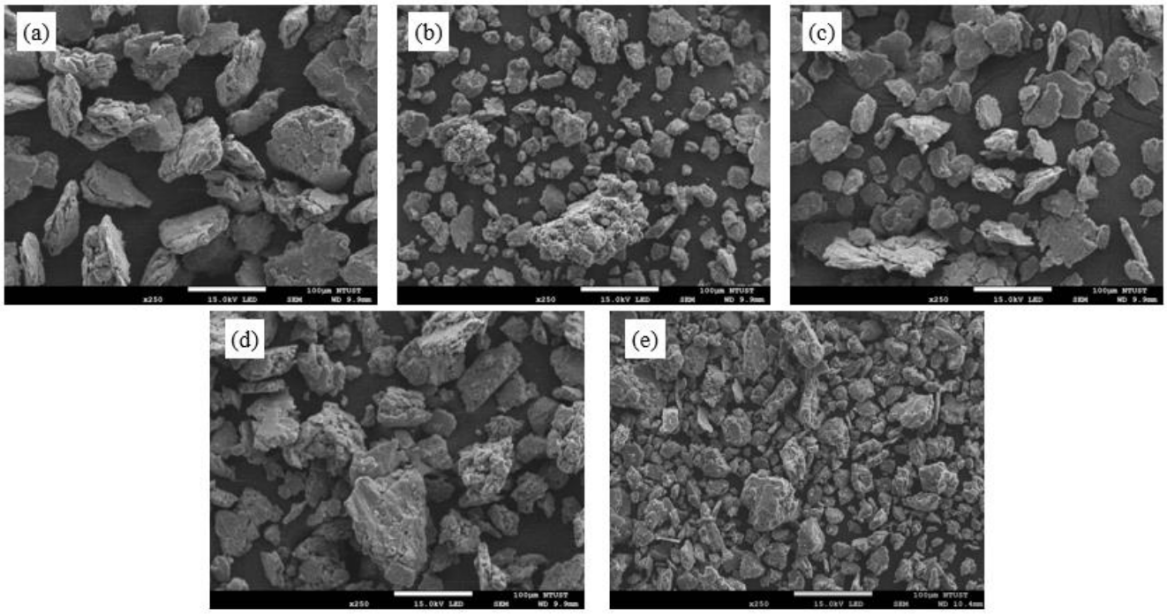


Figure 3: SEM images of (**a**) AZ31 (**b**) AZ31-0.1G (**c**) AZ31-0.2G (**d**) AZ31-0.1CNTs and (**e**) AZ31-0.2CNTs after HEBM-processed.

This outcome can be attributed to the superior physical properties of carbon materials monolayer structure. Serving as a grinding aid during ball milling, leading to a significant increase in the collision area during high-energy ball milling processes [20]. This results tells that the carbon additives can impact the particle size of the AZ-magnesium alloy. Furthermore, The average particle size of the ball-milled powder was been analyzed from SEM images via ImageJ software [19], which is shown in Table **1**.

Table 1: Average Particle Size of AZ31 with the Addition of Graphene and Carbon Nanotubes

Sample	Average particle size (μm)
AZ31-HEBM	64.5277
AZ31-0.1G-HEBM	29.8567
AZ31-0.2G-HEBM	39.2056
AZ31-0.1CNTs-HEBM	39.3556
AZ31-0.2CNTs-HEBM	33.4101

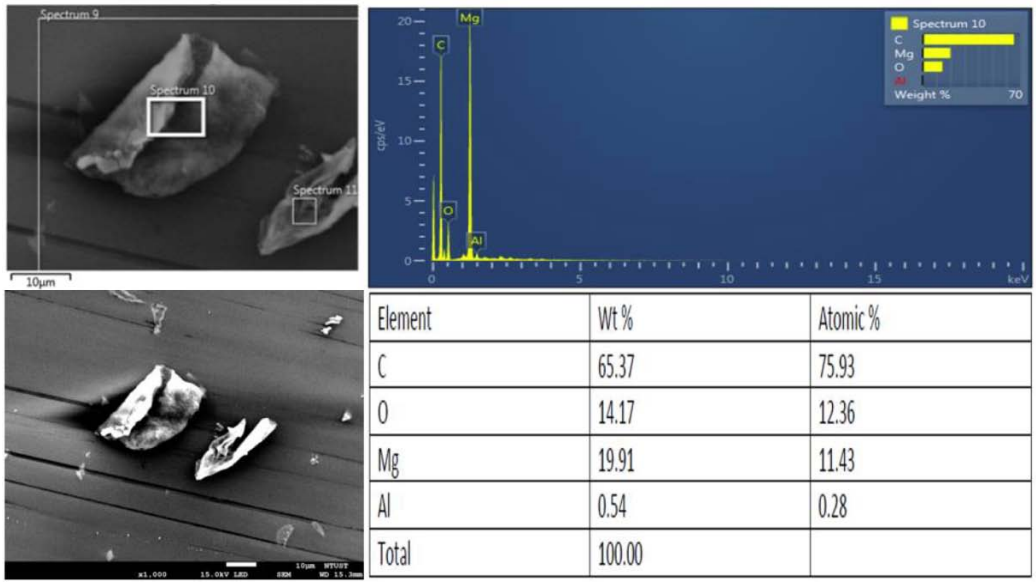
It is noticeable that there is an increasing trend in particle sizes for AZ31-0.1G and AZ31-0.2G as shown in Figure **2b** and **c**. The utilization of graphene with the lowest density ($0.025 g/cm^3$) in our study led to agglomeration issues during the casting process. This occurrence the inhomogeneous distribution of the graphene material, which failed to establish an energetic interface conducive to the nucleation of new grains throughout the casting process [15]. Consequently, it became evident that the particle size of AZ31-0.2G sample is larger compared to the AZ31-0.1G after HEBM with the same ball milling parameter.

In Figure **4**, the EDS results depict the elemental composition of the AZ31 magnesium alloy with 0.2 wt% graphene addition (AZ31-0.2G). The energy spectra of the selected area reveal the elemental compositions of Mg, Al, C, and O. The presence of graphene reached approximately 65.37 wt% concentrated confirmed the agglomeration occurred during the casting process.

3.3. Hydrogenation Kinetics

Figures **5a** and **5b** depict the hydrogenation kinetics curves integrating AZ31 magnesium alloy processed by high-energy ball milling (HEBM) with either carbon nanotubes or graphene. When compared to pure AZ31 magnesium alloy, the composite materials demonstrate heightened hydrogen absorption and desorption when reinforced with carbonaceous additives. Specifically, AZ31-0.1G (Graphene) displays remarkable absorption/desorption kinetic rates, surpassing those of other materials or pure AZ31. Notably, AZ31-0.1G exhibits accelerated hydrogen sorption kinetics, achieving an exceptional performance by absorbing 5.28 wt% of hydrogen in 1328 seconds and desorbing within 606 seconds, as shown in Table **2**.

The hydrogen storage properties of the sample materials are intricately connected to multiple factors, including the particle size, the heightened likelihood of



Element	Wt %	Atomic %
C	65.37	75.93
O	14.17	12.36
Mg	19.91	11.43
Al	0.54	0.28
Total	100.00	

Figure 4: EDS spectrum of AZ31-0.2G sample.

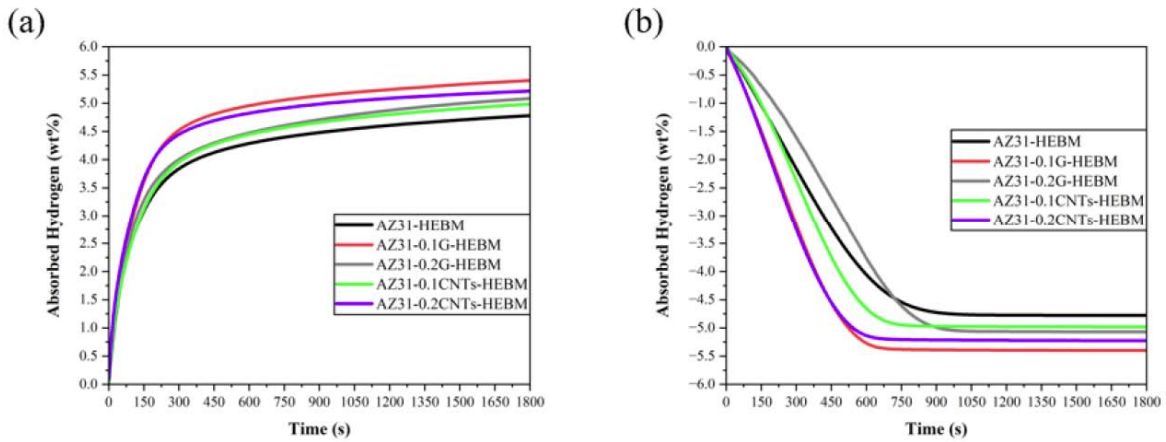


Figure 5: Hydrogenation kinetic curves for AZ31/carbon additives after HEBM-processed: (**a**) absorption and (**b**) desorption.

grain nucleation, and the defect density observed during the deformation process [14]. This collaborative refinement becomes especially pronounced when considering the material composition that incorporates 0.1 wt% graphene, notable for possessing the smallest particle size among all the samples with an average particle size of 29.8567 micrometers. The impact of this refined composition extends significantly, particularly during the hydrogenation process, where the unique characteristics of 0.1 wt% graphene play a pivotal role in influencing hydrogen storage dynamics. The small particle size and enhanced structural properties of this composition are poised to facilitate a more efficient and effective hydrogenation process, thereby contributing to the overall optimization of hydrogen storage capabilities in this specific material composition. This observation further underscores the adverse impact of increased particle size of AZ31-0.2G sample, indicating that larger particles do not contribute positively to the hydrogen storage property.

3.4. X-Ray Diffraction Analysis

XRD patterns of the AZ31-0.1G and AZ31-0.2G samples after hydrogenation are illustrated in Figure **6a** and **b**. Sample AZ31-0.1G exhibits prominent peaks corresponding to MgH_2 phases after absorption. However, in Figure **6b**, after conducting hydrogen absorption tests, the presence of Mg peaks for sample AZ31-0.2G indicates that the material has not undergone complete hydrogenation. Further hydrogen storage tests are still required. In Figure **6a**, the lower peak of Mg phases observed in AZ31-0.1G suggests that this alloy may have a more refined particle size, thereby offering increased surface area for hydrogen absorption. Additionally, the higher peak of MgO

Table 2: Average Hydrogen Absorption and Desorption Kinetics of AZ31/Carbon Powders Processed by HEBM

Sample	Temperature 375 (°C)			
	Hydrogen absorption capacity (wt%)	Hydrogen absorption rate (wt%/s)	Hydrogen desorption capacity (wt%)	Hydrogen desorption rate (wt%/s)
AZ31	4.69	0.0031	4.69	0.0054
AZ31-0.1G	5.32	0.0036	5.32	0.0084
AZ31-0.2G	4.98	0.0034	4.98	0.0056
AZ31-0.1CNTs	4.89	0.0033	4.89	0.0070
AZ31-0.2CNTs	5.15	0.0035	5.15	0.0080

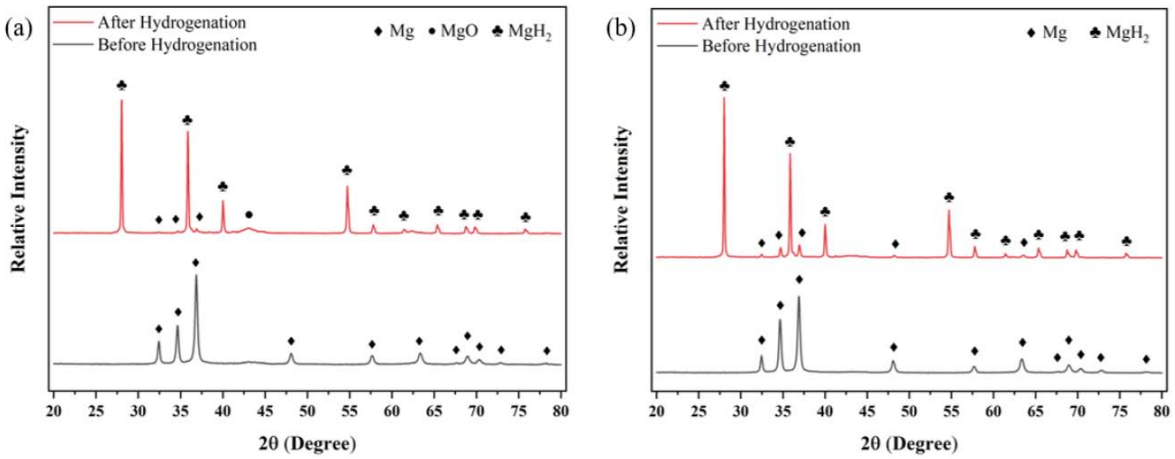


Figure 6: XRD patterns of (**a**) AZ31-0.1G and (**b**) AZ31-0.2G.

phases for AZ31-0.1G in the same figure may further suggest that the alloy's more refined particle size makes it more susceptible to oxidation.

Through XRD analysis, we can demonstrate that the experimental material with 0.1 wt% graphene exhibits superior hydrogen storage performance compared to the material with 0.2 wt% graphene. This is attributed to the findings mentioned above.

4. CONCLUSION

In our research, we examined the hydrogen storage performance of an industrial waste-grade AZ31 magnesium alloy combined with either Carbon Nanotubes or Graphene, utilizing the gravity casting method. The primary objective of this study is not only to compare but also to enhance the hydrogen storage properties through the reinforcement with polymer materials, such as Graphene or Carbon Nanotubes, coupled with the high-energy ball milling process.

1. During high-energy ball milling process, the addition of carbonaceous material effectively improves the particle size refinement for the AZ31 metal alloy. Among the samples, AZ31-0.1G stands out with the smallest particle size. As a result, the absorbed and desorbed hydrogen capacity, along with kinetics, show that AZ31-0.1G exhibits the highest absorption and desorption rates at 0.0036 wt%/s and 0.0084 wt%/s. Moreover, the hydrogen capacity reached at 5.32 wt%.

2. The reduction of particle size significantly affects hydrogen storage properties. As the particle size becomes finer, there is an enhancement in hydrogen capacity. This improvement is attributed to the creation of a substantial number of defects, a consequence of reducing the particle size, which subsequently increases the surface area available for hydrogen interaction.

3. The casting process experienced graphene agglomeration due to the low density of graphene (0.025 g/cm^3). In the case of AZ31-0.2G sample, the consequences lead to a diminished collision area during high-energy ball milling processes. The EDS results in Figure **4** further illustrate the elemental composition of

AZ31-0.2G, with a notable concentration of approximately 65.37 wt% carbon, indicating graphene agglomeration during casting. Consequently, it fails to influence the particle size refinement during ball milling.

4. The acquired data reveals that the addition of either Graphene or Carbon Nanotubes as additives significantly enhances the overall hydrogen storage capacity of AZ31 magnesium alloy.

DECLARATION OF INTEREST STATEMENT

The authors declare that there isn't any conflict of interest with regard to the current study.

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