

The effects of graphite additive on hydrogen sorption/desorption behavior by the Mg/C composite

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Abstract: The reactive ball milling technique was applied to fabricate the Mg-based composite with graphite additives. The sorption/desorption kinetics of the composites were investigated under isothermal conditions. The best hydrogen sorption/desorption kinetics was attained for the magnesium-carbon composite synthesized using the low surface area graphite powder as an active additive. This sample is characterized by the best kinetics performance compared to other composites. It releases 4.2 wt.% of hydrogen at 270 °C within ~18 min and uptakes 4.6 wt.% of hydrogen for ~130 min at 200 °C.

Keywords: HYDROGEN STORAGE, Mg, GRAPHITE ADDITIVE, SORPTION/DESORPTION

1. Introduction

The most ecologically clean source of energy is hydrogen. Its combustion in the heated element leads only to the formation of water, which prevents pollution of the environment by combustion products. However, several drawbacks prevent the widespread use of hydrogen. One of these obstacles is the development of efficient and safe hydrogen storage systems, which is associated with its low density (gaseous state ~0.09 kg/m³), low liquefaction temperature, and high explosiveness [1]. The requirements of the US Department of Energy (DOE) are guided during the development of promising hydrogen storage systems [2]. There are several ways of storing and transporting hydrogen [3, 4], namely in:

- a gaseous state under pressure (high pressure cylinders);
- a liquid state in cryogenic containers;
- the solid-phase bound state in metal hydrides;
- an adsorbed state on cryoadsorbents at low temperatures;
- a chemically bound state in liquid media;
- combined systems.

However, none of the above hydrogen storage methods meets the requirements of the Department of Energy. Developing a safe, efficient, and cost-effective way to store hydrogen is an important task.

The metal/intermetallic hydrides are the most suitable and promising method to store and transport hydrogen in large amounts. Some of these compounds have fast hydrogen uptake/desorption kinetics at near-ambient temperatures, a simple activation process, and moderate hydrogenation pressure. However, most of them have a low hydrogen capacity [5-8].

One of the most promising candidates for long-term hydrogen storage and transport is magnesium due to its high theoretical reversible hydrogen storage capacity (7.6 wt. %) and low cost [9]. Moreover, magnesium is widely distributed in nature, non-toxic and safe to use when preventing its oxidation. The equilibrium modification of MgH₂ is a tetragonal α -MgH₂ phase. Under the high pressure impact, α -MgH₂ undergoes polymorphic transformations with the formation of two modifications: γ -MgH₂ and β -MgH₂, which have a rhombic structure and a hexagonal structure, respectively [10]. However, some drawbacks limit the practical use of MgH₂ as a hydrogen storage medium. These include high values of operating temperatures ~300 °C, slow sorption/desorption kinetics, difficulty of activation, and deterioration of properties during cycling [11]. Various methods have been offered to overwhelm the disadvantages pointed out above. The mechanical activation of magnesium with various additives/catalysts attracts particular attention. The mechanical activation process provides the controllable synthesis of the nanosized materials distinguished by "softer" hydrogen sorption/desorption modes. The catalytic additives significantly reduce the operating temperatures and facilitate the kinetics of interaction between hydrogen and magnesium [12-18], also.

In this paper, we used graphite powders with different specific surface areas as an active additive to magnesium. The samples were synthesized by reactive ball milling under a hydrogen atmosphere.

2. Materials and method

The reactive ball milling technique under hydrogen (Fritsch Pulverisette P-6 ball mill) was applied to fabricate Mg-based composites. A special stainless steel milling bowl was designed to execute the mechanical activation procedure under a high-pressure hydrogen medium. The composition of the samples and specific surface area values ($S_{\text{BET}}(\text{C})$) of the used graphitic powders are listed in table 1. The total duration of ball milling process for all samples was 30 hours. The milling process was divided into 15 min intervals to prevent the grinding container from overheating. Every 15 min milling interval was followed by a 1 min pause. The speed of rotation of the grinding container (n) and the ratio of the mass of the balls to the mass of the powder ($m_b : m_p$) were unchanged in all experiments and were $n = 400$ rpm. and $m_b : m_p = 30 : 1$, respectively. X-ray diffraction studies are carried out on the standard diffractometer with filtered Co K α radiations in the Bragg-Brentano geometry. The interaction of magnesium-based composites with hydrogen was investigated on a homemade Sievert-type apparatus under isothermal conditions.

Table 1: Chemical composition of samples.

Sample №	The composition of the composite, wt. %		$S_{\text{BET}}(\text{C})$, m ² /g
	Mg	C (graphite)	
Mg-C0	100	-	-
Mg-C1	90	10	8,135
Mg-C2	90	10	329

3. Result and discussion

The XRD patterns of as-milled Mg-based composite are shown in Fig. 1.

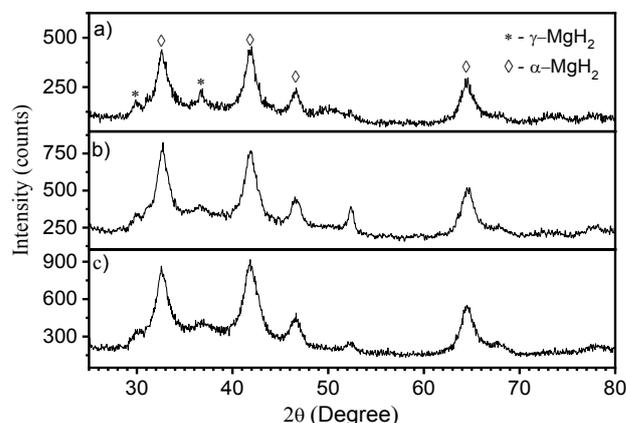


Fig. 1 XRD pattern of as-milled Mg-based composite: a – Mg-C0; b – Mg-C1; c – Mg-C2.

It should be noted the all samples have wide diffraction maximums with positions close to γ -MgH₂ and α -MgH₂ phases. It has been found by the Rietveld refinement procedure the graphite-free sample (Fig. 1, a) contains two phases: ~ 63 wt.% of α -MgH₂ and ~ 37 wt.% of γ -MgH₂. The crystallite sizes are 150 and 100 Å for α -MgH₂ and γ -MgH₂, respectively. Graphite additive with the 8.1 m²/g surface area to magnesium leads to decreases ~ 53 wt.% of α -MgH₂ phase in a composite Mg-C1 (Fig. 1, b). However, the percentage of the γ -MgH₂ phase in the Mg-C1 sample rises to ~47 wt.%. The crystallite size for α -MgH₂ and γ -MgH₂ hydrides are 100 and 30 Å, respectively. The Mg-C2 composite which contains graphite additive with the 329 m²/g surface area has ~ 60 wt.% of α -MgH₂ and ~ 40 wt.% γ -MgH₂ phase (Fig. 1, c). The crystallite size for both phases is 100 Å.

The hydrogen sorption/desorption kinetics of the Mg-based composites was examined under isothermal conditions by Sievert's technique for as-milled and activated samples at 300 and 270 °C, respectively. Kinetics measurements were executed for the temperatures when the fastest hydrogen uptake/release processes were.

Fig. 2 shows the hydrogen desorption curves at 300 °C for the as-milled Mg-C composites and pure Mg.

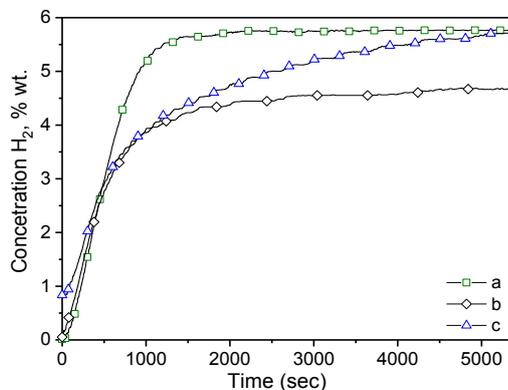


Fig. 2 Desorption of hydrogen in isothermal conditions at $T=300$ °C for as-milled composites: a – Mg-C0; b – Mg-C1; c – Mg-C2.

It is clear, that the best hydrogen kinetics and capacity are for the as-prepared graphite-free sample Mg-C0 (see Fig. 2, a). This sample desorbs 5.7 wt.% of hydrogen within 30 min at 300 °C. In contrast to the graphite-free sample, the graphite-containing ones show sluggish hydrogen release kinetics. So, the graphite containing samples Mg-C1 (Fig. 2, b) and Mg-C2 (Fig. 2, c) desorb 4.65 wt.% and 5.7 wt.% of H₂ more than twice slower for 80 and 85 min, respectively. It is worth noting that as-prepared composites Mg-C1 and Mg-C2 can release less hydrogen capacity and exhibit worse kinetics compared to pure magnesium.

After the activation of the samples, the behaviour of the hydrogen desorption curves is significantly different from the non-activated ones. Fig. 3 shows the hydrogen desorption curves recorded for the activated samples at 270 °C. A catalytic effect of graphite additive with different specific surface areas on the desorption process is noticeable. It can be seen that graphite less sample Mg-C0 (Fig. 3, a) at this temperature can desorb ~4.64 wt.% hydrogen for 57 min. Under the same conditions, Mg-C2 composite releases ~4.6 wt.% hydrogen within 59 min (Fig. 3, b). Thus, it is clear that the graphite powder with a specific surface area of 329 m²/g affects the hydrogen desorption kinetics negligibly. The composite Mg-C1 with a small surface area of graphite additive ~8.1 m²/g demonstrates an increased rate of dehydrogenation compared to other samples (Fig. 3, c). Under isothermal conditions, this sample releases ~4.2 wt.% of H₂ at 270 °C within 18 min.

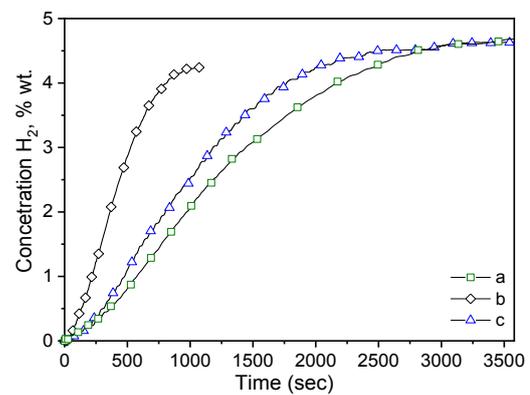


Fig. 3 Desorption of hydrogen in isothermal conditions at $T=270$ °C for activated composites: a – Mg-C0; b – Mg-C1; c – Mg-C2.

The studies of the hydrogen sorption kinetics under isothermal conditions at a temperature of 200 °C have been carried out (Fig. 4).

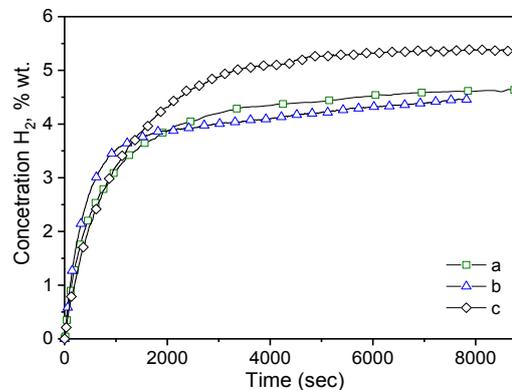


Fig. 4 Sorption of hydrogen in isothermal conditions at $T=200$ °C for activated composites: a – Mg-C0; b – Mg-C1; c – Mg-C2.

The maximum hydrogen storage capacity absorbed by Mg-C0 and Mg-C1 samples within 130 min is about 4.6 wt.% and 4.4 wt.%, respectively (Fig. 4, a and b). The composite Mg-C2 was saturated at a rate higher than Mg-C0 and Mg-C1 samples and reached a higher hydrogen capacity. It was found the Mg-C2 composite with graphite powder (329 m²/g) uptakes 5.3 wt.% of hydrogen for 90 min (Fig. 4, c).

4. Conclusion

The Mg-C composites applying graphite powders with different specific surface areas (8.1 and 329 m²/g) were produced by reactive ball milling technique in a hydrogen gas atmosphere. It was uncovered the surface areas of the graphite powder added to magnesium affect the hydrogen sorption/desorption kinetics of the Mg-based composites. The Mg-C1 composite (surface area of graphite is 8.1 m²/g) shows the best hydrogen desorption kinetics. This sample releases ~4.2 wt.% of H₂ at 270 °C within 18 min. Also, the hydrogen sorption curves recorded under isothermal conditions for the 200 °C were analysed. It has been clarified that the Mg-C2 sample (surface area of graphite is 329 m²/g) uptakes ~5.3 wt.% of H₂ within 90 min at 200 °C.

5. Acknowledgments

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6. References

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