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High-temperature hydrogen cycling properties of magnesium-based composites

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ABSTRACT

High-temperature desorption kinetics and cyclic stability of MgH_2-TM composites (TM=Fe, Co) were studied to investigate the feasibility of the composites as thermal energy storage materials. At 420 °C and 440 °C, the desorption kinetics of MgH_2 can be significantly improved by adding 5 wt% of nanosize Fe or Co. At 420 °C, MgH_2-Fe and MgH_2-Co composites have excellent cyclic stability with a hydrogen storage capacity of 7.0 wt%. While cycling at 440 °C, the MgH_2-Co shows a poor cyclic stability with a lower storage capacity of 5.0 wt%. The capacity loss is the result of formation of MgCo and Mg_2CoH_5 during the cycling process.

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1. Introduction

Magnesium hydride (MgH_2) with a high energy storage density (2814 kJ/kg) is a potential candidate for high-temperature thermal energy storage (TES), which plays an important role in concentrating solar thermal (CSP) power and industrial waste-heat recovery applications [1–3]. However, MgH_2 is well known for its sluggish hydrogen absorption and desorption kinetics, which hinders its practical use. One solution to the problem is to combine MgH_2 with additives [4–8].

Transition metals (TM) are promising additives to enhance the reaction kinetics of MgH_2 [8–10]. However, most of the studies are focused on the low-temperature hydrogen storage for PEM fuel cell applications. Little has been done in the study of MgH_2 for its high-temperature properties needed for TES systems, including desorption kinetics and cyclic stability. Bogdanović et al. reported high-temperature cyclic stability of MgH_2-Ni composite. Upon cycling at 480 °C, irreversible capacity loss due to the Mg-Ni eutectic reaction (at 506 °C) was observed [11]. In this work, we combined MgH_2 with TMs that do not have eutectic reactions with Mg or have higher eutectic temperatures than that of Mg-Ni. Two TM additives, Fe and Co, were selected. The high-temperature hydrogen desorption kinetics and cyclic stability of the hydride composites were investigated.

2. Material and methods

Mg-based hydride composites were prepared by mechanical milling of MgH_2 (~98 wt%) with 5 wt% of Fe (particle size ~25 nm) or Co (particle size ~28 nm) nanoparticles for 4 h under argon in a planetary ball mill. The as-milled MgH_2 was labeled as MgH_2-BM, while the prepared composites were labeled as MgH_2-5TM with TM=Fe, and Co. Characterization of powders was conducted with a scanning electron microscope and by X-ray diffraction. The specific surface area and the apparent activation energy of dehydrogenation were measured. Hydrogen storage properties of hydride composites were evaluated by performing cycle tests at 375, 420 and 440 °C. The absorption kinetics were measured at under 8 MPa of hydrogen; while the desorption kinetics were measured under 0.1 MPa of hydrogen. After the final absorption, the sample cell was quenched into water under hydrogen pressure until it reached room temperature. The sample was analyzed by XRD to identify the phases after hydrogenation (see Supplementary material for details).

3. Results and discussion

The representative morphology of the as-received and as-milled MgH_2 is shown in Fig. 1 (the morphology of the as-milled composites is similar to that given in Fig. 1b). The powders are well refined after 4 h of milling. The results of EDS mapping show that Fe and Co additives were distributed uniformly (see Fig. S1 for the morphology and EDS mapping of as-milled composites). XRD analysis indicates the presence of β–MgH_2 phase in all of the as-

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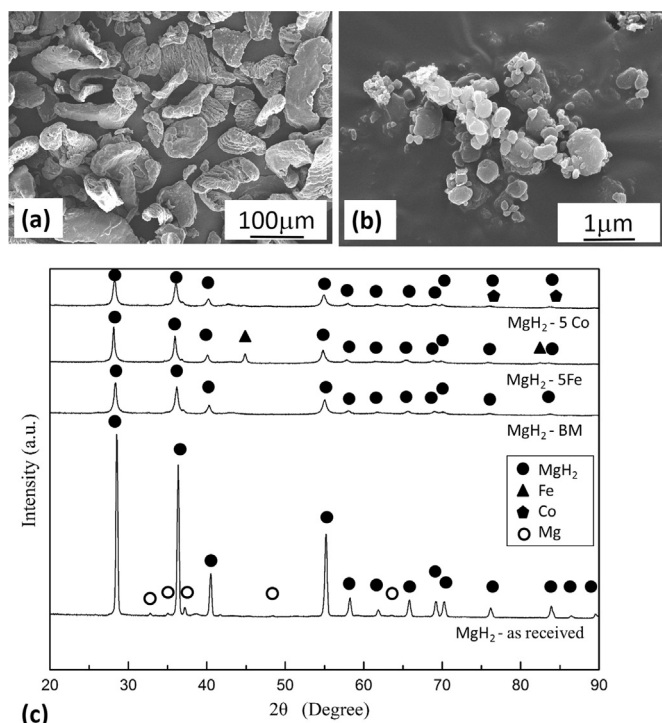
Fig. 1. SEM images of (a) as-received MgH_2 powder and (b) as-milled MgH_2. (c) XRD patterns of as-received MgH_2, as-milled MgH_2 and composites.

milled powders (Fig. 1c). Mg-TM and Mg-TM-H phase are not formed after milling. The XRD-calculated crystallite size of MgH_2 in the as-milled powders is between 15 and 25 nm. Specific surface area of the as-milled powders ranges from 11 to 13 m^2/g. Adding Fe and Co additives does not significantly change the crystallite size and specific surface area of the as-milled MgH_2.
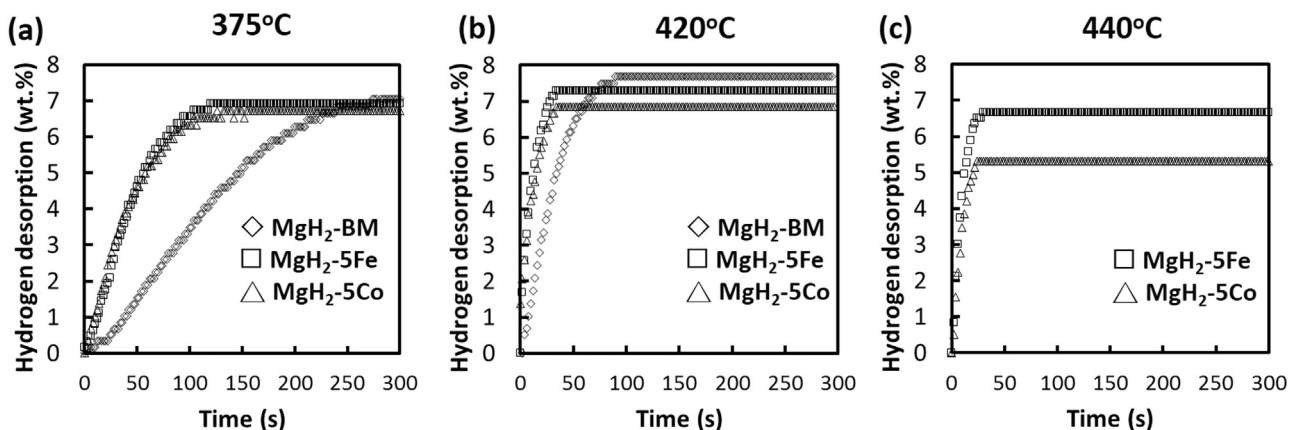
Fig. 2 shows the first cycle hydrogen desorption kinetics of the as-milled powders. At 375 °C, the composites show a pronounced improvement on desorption kinetics. The results are similar to other studies reported for the effect of Fe and Co on desorption of MgH_2 at temperatures lower than 400 °C [10,12]. At 420 and 440 °C, adding of Fe and Co also enhances the desorption kinetics of MgH_2. There is no big difference in the desorption kinetics between the MgH_2-5Fe and MgH_2-5Co. The apparent activation energies of MgH_2-BM, MgH_2-5Fe and MgH_2-5Co are 136, 50, and 66 kJ/mol, respectively (Fig. S2). The smaller activation energies of MgH_2-TM composites indicates higher desorption kinetics. The results agree well with the observed desorption kinetics. Fig. 3 shows the cyclic stability of the as-milled powders. The excellent

cyclic stability of MgH_2-5Fe at a hydrogen storage capacity of about 7.0 wt% can be observed at 375, 420 and 440 °C (Fig. 3a). While the excellent cyclic stability at a capacity level about 7.0 wt% is found in the MgH_2-5Co at 375 and 420 °C, capacity decreases to about 5.0 wt% after 5 cycles of test at 440 °C (Fig. 3b).

To explain the difference in the cyclic stability between the MgH_2-5Fe and MgH_2-5Co at 440 °C, XRD analysis of the cycled composites was performed. As shown in Fig. 4, no Mg-Fe and Mg-Fe-H phase are formed after cycling at 375 and 420 °C. The phases are mainly β-MgH_2 and a small amount of Fe. A small amount of MgO is also observed. However, when the temperature increases to 440 °C, a small amount of Mg-Fe-H phase (Mg_2FeH_6) is formed. Fig. 4 also shows the presence of Mg, MgCo and Mg_2CoH_5 phases [13] in the MgH_2-5Co powders after cycling at 420 and 440 °C. The peak intensities of latter two phases do not show visible changes with temperature. However, the peak intensities of Mg phase at 440 °C are stronger than those at 420 °C, indicating that the composite after cycling at 440 °C contains more unreacted Mg (Fig. S3).

Peak intensities of MgO in the MgH_2-5Fe and MgH_2-5Co powders after cycling at different temperatures are similar, indicating that the amounts of MgO are similar. The presence of MgO is not the reason causing the difference in the cyclic stability. The possible reasons that might lead to a capacity loss in MgH_2-TM composites can be summarized as following: (1) the additive in the hydride composite do not absorb hydrogen. (2) The additive reacts with MgH_2 during the milling process. The newly formed product has a lower storage capacity than that of MgH_2 or it does not absorb hydrogen. (3) The additive reacts with MgH_2 during the absorption process or with Mg during the desorption and the vacuum process. The product does not absorb hydrogen or has a lower hydrogen capacity than that of MgH_2. (4) Remnant Mg, which is not able to react with hydrogen to form MgH_2.

Mg-TM, and Mg-TM-H phases are not observed in the as-milled composites, hence the reason (2) can be excluded. After cycling at 375 °C, Fe and Co do not react with hydrogen to form Fe-H, Co-H hydrides. Mg-Fe-H and Mg-Co-H hydrides are also not synthesized. No remnant Mg is detected in the MgH_2-5Fe composites cycled at all temperatures and the MgH_2-5Co composite cycled at 375 °C. Compared to the storage capacity of MgH_2, the storage capacities of the MgH_2-5Fe and MgH_2-5Co powders decrease slightly. This can be attributed to reason (1). When cycling temperature increases to 420 °C, Mg-Fe intermetallic phase, Fe-H and Mg-Fe-H hydrides are not formed in the MgH_2-5Fe composite. The reason that storage capacity drops is reason (1). Further increasing cycling temperature to 440 °C leads to the formation of Mg_2FeH_6 phase, which stores less hydrogen than MgH_2 does. The reason that storage capacity drops can be concluded to be reason (3).

Fig. 2. First cycle hydrogen desorption kinetics of the as-milled MgH_2 and composites at (a) 375, (b) 420, and (c) 440 °C.