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Synergy of elemental Fe and Ti promoting low temperature hydrogen sorption cycling of magnesium

Babak Shalchi Amirkhiz^{a,b,*}, Beniamin Zahiri^{a,b}, Peter Kalisvaart^{a,b}, David Mitlin^{a,b}

^aDepartment of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada

^bNational Institute for Nanotechnology, NRC, Edmonton, Alberta, Canada

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ABSTRACT

We studied the catalytic effects of Titanium, Iron and FeTi intermetallic on the desorption kinetics of magnesium hydride. In order to separate the catalytic effects of each element from additional synergistic and alloying effects, Mg–Ti and Mg–Fe mixtures were studied as a baseline for Mg–Fe–Ti elemental and Mg–(FeTi) intermetallic composites. Sub-micron dimensions for MgH₂ particles and excellent nanoscale catalyst dispersion was achieved by high-energy ball-milling as confirmed by analytical electron microscopy techniques. The composites containing Fe shows desorption temperature of 170 K lower than as-received MgH₂ powder, which makes it suitable to be cycled at relatively low temperature of 523 K. Furthermore, the low cycling temperature prevents the formation of Mg₂FeH₆. In sorption cycling tests, Mg-10% Ti and Mg-10% (FeTi), after about 5 activation cycles, show fast desorption kinetics initially, but the kinetics also degrade faster than for all other composites, eventually slowing down by a factor of 7 and 4, respectively. The ternary Mg–Fe–Ti composite shows best performance. With the highest BET surface area of 40 m²/g, it also shows much less degradation during cycling. This is attributed to titanium hydride acting as a size control agent preventing agglomeration of particles; while Fe works as a very strong catalyst with uniform and nanoscale dispersion on the surface of MgH₂ particles.

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1. Introduction

Magnesium hydride stores a large amount of hydrogen (7.6 wt.%) reversibly, but suffers from very slow kinetics and high thermodynamic stability (–76 kJ/mol H₂), both necessitating high temperatures around 573 K for desorption. Many attempts have been made to alter the thermodynamics of magnesium hydride by incorporating alloying elements such as Ni, Cu, Al and Si [1–7], but no viable way to produce large quantities of destabilized material has been found. As a consequence, most research efforts have been directed at improving the sorption kinetics of magnesium hydride.

Transition metals in particular have been intensively studied theoretically and experimentally as suitable catalysts for sorption of magnesium (hydride) [8–16]. It has been shown that co-milling 3d-metal catalysts with MgH₂ may result in lower activation energies and faster sorption kinetics; however the thermodynamics remains unchanged [9–12,17].

Fe has been proposed as a strong catalyst towards hydrogen sorption of magnesium [10,12,18–21]. It is visually shown, with the aid of SEM, that the kinetics of MgH₂ desorption changes drastically in the presence of Fe catalyst particles; the nucleation of Mg phase occurs in the interface of MgH₂ and Fe [22]. Besides, in Mg–Fe systems prolonged

* Corresponding author. Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada.

E-mail address: shalchi@gmail.com (B.S. Amirkhiz).

cycling at temperatures of higher than 573 K eventually resulted in formation of Mg_2FeH_6 [23].

Intermetallic compounds of transition metals are also considered as catalysts or destabilizing materials for magnesium (hydride). Efforts have been made to destabilize magnesium hydride by using intermetallic compounds with low heat of hydride formation; however, no significant change in the thermodynamics was achieved for these composites [20,21,24,25]. The FeTi intermetallic compound has also been investigated as a catalyst towards hydrogen sorption of magnesium [14,20,21,24–28]. FeTi directly reacts with hydrogen to form $\text{FeTiH}_{\sim 1}$ at room temperature and 10 atm hydrogen equilibrium pressure and form $\text{FeTiH}_{\sim 2}$ at higher but not well defined plateau pressure [29,30]. Nanocrystalline FeTi, can readily absorb hydrogen with no activation required [30].

A ternary magnesium based composite prepared by co-sputtering of magnesium, titanium and iron has exceptionally good cycling performance in terms of both the kinetics and stability against degradation compared to the baseline binary systems. These improvements are attributed to possible formation of a nano-crystalline/amorphous FeTi phase or synergistic catalytic effect of titanium and iron [14,31]. Most research efforts have been directed at improving the kinetics by mixing MgH_2 with different catalysts using high-energy ball-milling to achieve uniform dispersion of the catalyst. Moreover, it is known that milling has intrinsic effects on the activation energy for desorption and can reduce its value by up to 50% in the first desorption cycle. However, annealing treatment and prolonged absorption/desorption cycling eliminates these defects and increases the activation energy back to 150 kJ/mol [32]. Therefore, it is important to check the activation energies both in the as-milled and cycled state, as the catalysts effectiveness may be reduced or even completely lost during extensive cycling [33].

The present paper reports on the hydrogen cycling behavior of ball-milled MgH_2 -Ti, MgH_2 -Fe, MgH_2 -Fe-Ti and MgH_2 -FeTi mixtures. We characterize the dispersion of the catalyst before and after cycling to have a better understanding of the catalytic activity of each additive using elemental mapping of scanning transmission electron micrographs. The as-milled and as-cycled microstructure was characterized using X-ray diffraction. We incorporated differential scanning calorimetry (DSC) and Sievert's techniques to assess the desorption activation energies in both as-milled and cycled states, and sorption cycling kinetics. We employ JMA kinetics model to track the kinetics and rate limiting mechanisms as a function of cycling for these composites.

2. Experimental techniques

Magnesium hydride (MgH_2) powder was 98% pure hydrogen storage grade purchased from ABCR GmbH Co. KG, the balance being magnesium. Titanium powder was 99.7% pure, < 150 μm average particle size purchased from Sigma-Aldrich®. Iron powder was 99% pure, < 212 μm average particle size purchased from Sigma-Aldrich®. FeTi intermetallic compound powder was high-purity with < 150 μm average particle size purchased from Goodfellow®.

We made two kinds of ternary composites by combining the hydride powders with 5 at.% Fe–5 at.% Ti and 10 at.% FeTi and we also made two binary composites of MgH_2 with 10 at.% Fe and 10 at.% Ti serving as the baseline. To achieve a reasonable dispersion of FeTi compound on MgH_2 particles we added 2.5 wt% multi-walled carbon nanotubes (MWCNTs) the beginning of the milling experiment. Equal amounts of FeTi and MgH_2 powders were ball-milled for 5 h and subsequently MWCNTs and more MgH_2 were added up to make the composition MgH_2 -10 at.% (FeTi)-2.5 wt% CNTs. For the sake of brevity we use the following nomenclature for these composites throughout the manuscript: MgH_2 -5 at.% Fe-5 at.% Ti as MgH_2 -Fe5Ti5, MgH_2 -10 at.% (FeTi)-2.5 wt% CNTs as MgH_2 -(FeTi)10, MgH_2 -10 at.% Fe as MgH_2 -Fe10 and MgH_2 -10 at.% Ti as MgH_2 -Ti10. Except for MgH_2 -(FeTi)10, all the mixtures were milled for 10 h in a Fritsch Pulverisette 6 planetary monomill. We used a 10:1 ball to powder weight ratio, with agate balls and vial at 600 rpm rotation speed for all the composites. Milling and all sample handling were performed inside a high-purity argon filled glovebox with the amount of oxygen and water vapor present being less than 0.1 ppm.

We used a combined differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA) (SDTQ600, TA Instruments) to determine the hydrogen desorption kinetics and activation energy measurements. The analysis was performed under a constant flow of high-purity (99.998% pure) argon to prevent oxidation. A small sample of about 10 mg from each composite was transferred to a calorimeter right after milling. To maintain minimum exposure to air the transferring of the samples were performed using 90 μl alumina sample cups with alumina lids on (both cups and lids are purchased from TA Instruments).

Volumetric absorption and desorption measurements and also PCT measurements were performed using a Sievert's hydrogen sorption analysis system (Hy-Energy LLC. PCTPro 2000). All of the cycling measurements were carried out at 523 K. The composite powders were analyzed aiming 100 + cycles and stopped earlier when degradation was apparent. Absorption started at a pressure of 0.25 MPa (finishing at around 0.1 MPa) and desorption at a starting pressure near 0.001 MPa (finishing at 0.002 MPa). The sample holder is inserted in an aluminum cylinder to provide fast heat exchange. The cylinder is surrounded by a heater which is in turn covered with an insulating jacket. Because of the sample size, approximately 30 mg, the total heat capacity of the system is very large compared to the amount of heat produced during absorption. The temperature variations during absorption and desorption, as measured by a thermocouple inserted into the sample holder directly beneath the sample powder, are within ± 1.5 K.

Transmission electron microscopy (TEM) was performed using the JEOL 2200FS microscopes, operating at 200 kV accelerating voltage. Scanning transmission electron microscopy (STEM) with a probe of a diameter of 1 nm was used. We used a high-angle annular detector to form high-angle annular dark field (HAADF) images where the contrast is directly related to the atomic number Z. This technique coupled with energy-dispersive X-ray spectroscopy (EDS) with the capability of forming elemental maps was used to study the distribution of the catalyst material on magnesium

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