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Magnesium–carbon hydrogen storage hybrid materials produced by reactive ball milling in hydrogen

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ABSTRACT

Time-resolved studies uncovered kinetics and mechanism of Mg–hydrogen interactions during High energy reactive ball milling in hydrogen (HRBM) in presence of various types of carbon, including graphite (G), activated carbon (AC), multi-wall carbon nanotubes (MWCNT), expandable (EG) and thermally-expanded (TEG) graphite. Introduction of carbon significantly changes the hydrogenation behaviour, which becomes strongly dependent on the nature and amount of carbon additive. For the materials containing 1 wt.% AC or TEG, and 5 wt.% MWCNT, the hydrogenation becomes superior to that for the individual magnesium and finishes within 1 h. Analysis of the data indicates that carbon acts as a carrier of the "activated" hydrogen by a mechanism of spill-over. For Mg–G the hydrogenation starts from an incubation period and proceeds slower. An increase in the content of EG and TEG above 1 wt.% results in the deterioration of the hydrogenation kinetics. The effect of carbon additives has roots in their destruction during the HRBM to form graphene layers encapsulating the MgH_2 nanoparticles and preventing the grain growth. This results in an increase of absorption–desorption cycle stability and a decrease of the MgH_2 crystallite size in the re-hydrogenated Mg–C hybrid materials (40–125 nm) as compared to Mg alone (180 nm).

1. Introduction

Magnesium dihydride MgH_2 is an attractive hydrogen storage material. It has a high reversible hydrogen storage capacity (7.6 wt.% H/~110 kg H/m^3); magnesium metal is inexpensive and abundant. At the same time, slow hydrogenation/dehydrogenation kinetics at temperatures below 350 °C and high stability (that corresponds to an equilibrium hydrogen pressure of 1.0 bar at $T \sim 300$ °C) are the major obstacles for hydrogen storage applications on the basis of MgH_2. Numerous studies have been carried out in an effort to enhance Mg hydrogenation rate [1]. One of the most promising approaches was found to be mechanical milling (MM).

MM yields nanostructured materials with improved hydrogenation–dehydrogenation kinetics because of the modification of composition and structure. In particular, it allows to produce mechanical alloy Mg–25% Fe which cannot be obtained by conventional metallurgical routes [2]. During MM a combination of a repeated cold welding and fracturing of the particles will define the ultimate structure of the powder. The product of the milling often exhibits unusual physical and chemical properties, and enhanced reactivity,

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in particular, with respect to hydrogen. The enhancements are especially pronounced for Mg-based materials where nanostructuring and surface modification result in a dramatic improvement of the hydrogenation kinetics [3]. High energy reactive ball milling in hydrogen atmosphere (HRBM) of Mg with catalytic additives has been proven to be the most efficient way to further improve the re-hydrogenation process [4,5]. Some materials, for example, containing the additive of BCC-V alloy, were characterised by exceptional performances during their re-hydrogenation, which started even at room temperature and, at optimal conditions, was completed in less than 1 min [5].

Earlier, studies of carbon-containing Mg-based hydrogen storage hybrid materials attracted special attention. Imamura et al. [6] showed that MM of Mg and graphite with organic additives (e.g. benzene, cyclohexene and cyclohexane) resulted in improvement of the hydrogenation kinetics and decrease of dehydrogenation temperature. MM (4–40 h long) resulted in generation of dangling carbon bonds in graphite, promoting the formation of C–H bonds and thus forming new hydrogen-storing sites. HRBM of graphite was shown to result in the formation of the hydrogenated carbon ($CH_{\sim1}$; 7.4 wt.% H) where H atoms were both intercalated into the graphite interlayers, and, also formed covalent C–H bonds [7]. Similar results confirming chemisorption of H (4–6 wt.% H) in HRBM graphite were presented in [8]; the presence of iron nanoparticles introduced from milling tools resulted in an increase of the amount of the chemically bound hydrogen [9].

Huot et al. [10] has earlier demonstrated that graphite significantly accelerates reactive synthesis of MgH_2 during an hour long ball milling in H_2 (300 °C, 4.0 bar) with the formed materials showing improved hydrogenation and dehydrogenation kinetics. The use of various carbon species (graphite, activated carbon, carbon black, carbon nanotubes, fullerenes, nanodiamonds and other forms of nanoscale carbon) ball milled with Mg or MgH_2 reduces hydrogen sorption temperature, improves kinetics and also prevents MgH_2 particle growth during the hydrogenation/dehydrogenation cycling [11–22]. The observed improvements are more pronounced in case of the reactive ball milling of Mg with carbon additives in hydrogen gas [17].

It was also shown that compacting of Mg-based hydrogen storage materials with expanded natural graphite (ENG; $\geqslant$10 wt.%) results in a significant improvement of radial thermal conductivity of the obtained composites [23,24] that allowed for their industrial-scale usage in hydrogen storage systems characterized by fast dynamics of hydrogen uptake and release [24]. At the same time, the information about influence of ENG and similar materials on hydrogenation and dehydrogenation performances of HRBM Mg is still missing.

Despite intensive studies of MM and HRBM of Mg-based hydrogen storage materials, including carbon-containing ones, have been performed, information about hydrogenation behaviour of the material during HRBM is scarce. Usually, the evolution of phase–structural changes in the material during the milling is carried out by periodic sampling of the material from the milling vial followed by XRD and other analyses; less often, hydrogen absorption during HRBM is monitored directly by pressure measurements in the milling vial [25,26]. Collecting such information for HRBM of Mg-based hydrogen storage materials with various carbon additives, together with the supplementary structural, morphological and dehydrogenation/re-hydrogenation data, would be of high value to improve understanding of the mechanism governing hydrogen sorption performances and, furthermore, would promote the development of highly-efficient lightweight hydrogen storage materials.

Our earlier publications concerning studies of magnesium-based HRBM materials were mainly focused on the performance of the materials during their re-hydrogenation and phase–structural characterisation [5,27]. This paper will present in-depth data on the studies of hydrogen absorption–desorption behaviours of the synthesised by HRBM Mg–C hybrid materials containing various types of carbon, including graphite (G), activated carbon (AC), multi-wall carbon nanotubes (MWCNT), expandable (EG) and thermally-expanded (TEG) graphite, $\geqslant$1 wt.%. These materials and their hydrides were prepared and studied using synchrotron and conventional X-ray diffraction (XRD), transmission (TEM) and scanning (SEM) electron microscopy, combined differential scanning calorimetry and thermogravimetric analysis (DSC/TGA), thermal desorption spectroscopy (TDS), and by probing the kinetics of hydrogen absorption. Emphasis is on the *in situ* studies of the mechano-chemical hydrogenation of Mg in presence of various carbon additives ($\leqslant$5 wt.%). The effects of HRBM on the hydrogenation rate, thermal decomposition and re-hydrogenation performances, phase composition and microstructural evolution of Mg was studied as related to the type of carbon additives. Influence of the pre-history of the sample, thermal and surface composition, on the dehydrogenation and re-hydrogenation performances was also in the focus.

2. Experimental

The materials used in the study included commercially available powders of magnesium (250…1200 μm, 99.8%), graphite ($\leqslant$20 μm, 99+%), expandable graphite (500 μm, 99.9 + %), YP-50F activated carbon (3…20 μm), and multi-wall carbon nanotubes (diameter (5…20)$\cdot 10^{-3}$ μm, length 10 μm, 90+%). Thermally expanded graphite was prepared by heating the expandable graphite to 900 °C in an open tube furnace, for 1 h. MgH_2 (Alfa Aesar, 98%) was used as a reference material in studies of the dehydrogenation and re-hydrogenation performances. Further details on starting materials are given in Supplementary information.

HRBM was performed in two types of planetary ball mills, Fritsch P6 and Retsch PM100, under hydrogen pressure (P_0 = 30 bar), at a rotation speed of 500 rpm. HRBM in Fritsch P6 mill was carried out using 80 ml hardened steel vial at balls-to-powder weight ratio (BPR) of 40:1 and 80:1 (sample weight 3 and 1.5 g, respectively). To monitor the hydrogenation process, the milling was periodically paused (typically in 20–30 min intervals) and the vial, after cooling to room temperature, was connected to a Sieverts-type apparatus and the pressure drop was measured; the vial was then refilled with hydrogen (30 bar), and milling was continued. HRBM in Retsch PM100 mill was performed in a 220 ml hardened steel vial equipped with pressure–temperature monitoring system