Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Short Communication

The role of morphology and severe plastic deformation on the hydrogen storage properties of magnesium

Alexandre Augusto Cesario Asselli[*], *Nicolas Bourbeau Hébert*, *Jacques Huot*

Hydrogen Research Institute, Université du Québec à Trois-Rivières, 3351 des Forges, Trois-Rivières, Québec, G9A 5H7, Canada

ARTICLE INFO

Article history:
Received 1 May 2014
Received in revised form
6 June 2014
Accepted 8 June 2014
Available online 4 July 2014

Keywords:
Hydrogen storage materials
Magnesium
Accumulative roll-bonding (ARB)
Filing

ABSTRACT

In this paper we report the role of morphology and severe plastic deformation on the hydrogen storage properties of magnesium. Samples were prepared in air at room temperature by accumulative roll-bonding, filing and a combination of both processes. Accumulative roll-bonding drastically refined the microstructure of magnesium but resulted in a limited hydrogen capacity. Filing accelerated the activation of magnesium without compromising hydrogen capacity. Combining both techniques enhanced or worsened the hydrogen storage properties depending on the processing sequence. These results are explained in terms of microstructure and morphology of the samples.

Introduction

Because of its high hydrogen capacity, magnesium hydride is considered for hydrogen storage applications [1]. The high enthalpy of hydride formation makes it also attractive for thermal energy storage [2]. On the other hand, the Mg/MgH_2 system requires high temperature of operation due to its thermodynamic stability and slow kinetics of hydrogen absorption/desorption. Another issue is the first absorption of magnesium (activation). The activation process is very slow, and requires high temperature and hydrogen pressure. These activation conditions result in a high production cost of the hydride.

To overcome these drawbacks some actions can be taken, such as: microstructure refinement, increase of specific surface area and use of catalysts [3]. These characteristics can be found in nanocrystalline and nanocomposite powders prepared by high energy ball milling (HEBM) [4–7]. However, the capital and operation costs of HEBM at industrial level could be very expensive [8]. Furthermore, Mg-based materials prepared by HEBM should be handled under inert atmosphere because they could be pyrophoric, and also to avoid a deterioration of their hydrogen storage properties due to oxidation [9]. Therefore, low cost and easily scalable techniques that could replace HEBM should be investigated.

In this context, severe plastic deformation (SPD) techniques, such as equal channel angular pressing (ECAP) [10–13]

* *Corresponding author*. Tel.: +1 819 376 5011x4460.
E-mail addresses: alexandre.cesario.asselli@uqtr.ca, asselli@gmail.com (A.A. Cesario Asselli).
http://dx.doi.org/10.1016/j.ijhydene.2014.06.042

and accumulative roll-bonding (ARB) [14–19], have been studied to process Mg-based materials for hydrogen storage applications. These SPD techniques introduce high plastic strain to produce ultrafine grained materials [20].

Some studies showed that processing MgH_2 by ARB leads to nanoscale grain refinement and enhances the kinetics of hydrogen absorption/desorption [21,22]. Moreover, ARB is effective to synthesize nanocomposites by adding transition metal [23] and oxide [24] catalysts into MgH_2 matrix. ARB was also investigated as a mean to improve the activation of magnesium and its alloys [12,14,16,18,19]. Fast activation was only reported when Mg was rolled with 10 wt. % of Pd [14] or when the rolled material was mixed with 5 wt.% of MgH_2 and then ball milled under Ar atmosphere for 30 min [18,19].

In the case of ECAP, Skripnyuk et al. [10] showed that the hydrogen desorption kinetics of a Mg–Zn–Zr alloy (ZK60) can be improved by this technique. Krystian et al. [13] also investigated the hydrogen storage properties of a ZK60 alloy processed by ECAP. They showed that the material had a long-term durability in a test of 1000 cycles of hydrogen absorption/desorption. Here it should be point out that the activation curves were not presented in these studies [10,13]. Another important remark is that the samples were comminuted to powder using a rasp before the measurements of hydrogen absorption/desorption. In both papers, the authors stated that filing with a rasp modifies the microstructure, but these modifications can be neglected because they are insignificant as compared to the ones introduced by ECAP. Nevertheless, filing increases the surface/volume ratio of the materials, which should have an impact on the kinetics of hydrogen absorption/desorption. This motivated us to investigate the individual and cooperative effects of filing and SPD on the activation of magnesium.

In this study, we report the hydrogen storage properties of magnesium processed by ARB, filing and a combination of both techniques. Initial results showed that refining the microstructure of magnesium by ARB and increasing its specific surface area by filing could result in faster activation [25]. In this paper a more thorough investigation is reported and the results are discussed in terms of microstructure and morphology of the processed materials.

Experimental procedure

As starting material we used an as-cast ingot of magnesium from Norsk Hydro. Small plates with approximate dimension of 0.8 × 20 × 30 mm were cut off from the ingot and processed by ARB, filing or a combination of both processes. Four samples were prepared: (1) rolled plate; (2) filings from the ingot;

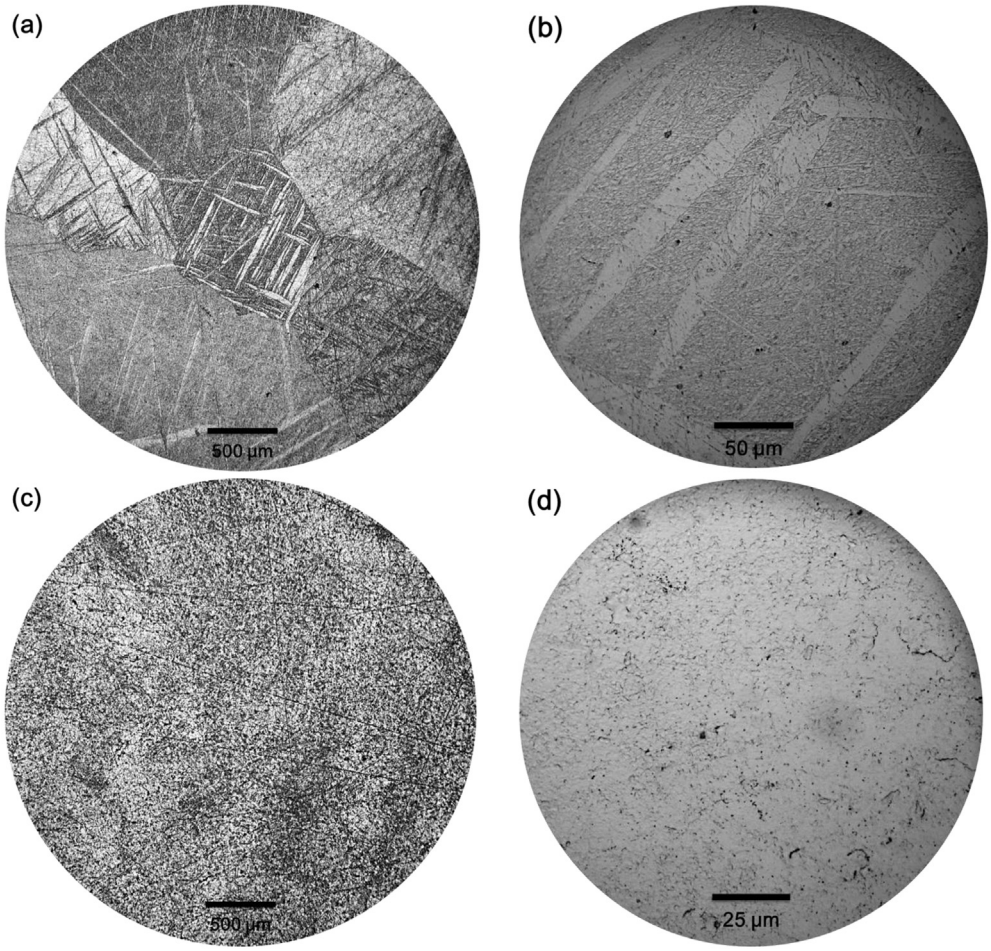

Fig. 1 – Optical micrographs of magnesium in as-received (a, b) and ARB processed (c, d) states.