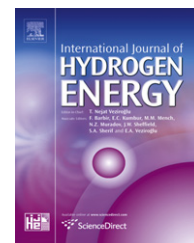


Available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/hydro

Effect of C (graphite) doping on the H₂ sorption performance of the Mg–Ni storage system

C. Milanese^{a,*}, A. Girella^a, S. Garroni^b, G. Bruni^a, V. Berbenni^a, P. Matteazzi^c, A. Marini^a

^a C.S.G.I. – Dipartimento di Chimica Fisica “M. Rolla”, Università degli Studi di Pavia, Viale Taramelli 16, 27100 Pavia, Italy

^b Dept. Física, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain

^c C.S.G.I. & MBN Nanomaterialia SpA, Via G. Bortolan 42, 31050 Vascon di Carbonera (TV), Italy

ARTICLE INFO

Article history:

Received 17 September 2009

Received in revised form

13 November 2009

Accepted 14 November 2009

Available online 23 December 2009

Keywords:

Hydrogen storage

Mg–Ni–C composites

Sorption kinetics

High-energy ball milling

X-ray powder diffraction

Calorimetric measurements

ABSTRACT

Binary Mg–Ni mixtures and ternary Mg–Ni–C (graphite) samples with fixed proportions of metals (Mg 85%–Ni 15% by weight) and amount of C increasing in increments of 5 wt % from 5 wt % to 15 wt % were prepared by high energy ball milling (BM) in Ar for $t_{BM} = 2$ h. The purpose of the study was to evaluate the effect of C addition on the reactivity, the sorption activation and the storage performance of the Mg–Ni system.

Increasing the amount of C had the effect of decreasing (from 10 to 3) the number of cycles needed for activation (performed at 623 K and 40 bar/0.9 bar charging/discharging H₂ pressure). After full activation, the 5 wt % C-containing sample exhibited the best absorption kinetics performance: the average rate to charge up to 5 wt % H₂ was about 3 times higher than that observed for the undoped sample. Unfortunately, increasing the amount of C had a negative impact on the desorption behaviour, causing an increase in the dehydrogenation activation energy and a decrease in the discharging rates.

Within the present study, C reacted neither with H₂ nor with the H₂ active phases (the two discharged phases Mg and Mg₂Ni and the related hydrides) and consequently did not lead to variation in the sorption enthalpies of the Mg–Ni system. But, its presence did cause a small increase (4 K at 0.9 bar H₂) in the minimum desorption temperatures of the hydrides and a consequent minor decrease (0.2 bar) in the equilibrium pressures.

The best sorption properties were obtained for the 5 wt % C-sample, that on the whole worked better than the binary mixture.

© 2009 Professor T. Nejat Veziroglu. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Metallic hydrides are currently the subject of several intensive energy research activities all over the world [1]. In particular, MgH₂ satisfies most of the requirements needed for approving its use as a hydrogen storage material in stationary as well as in mobile applications [2,3] thanks to its high theoretical gravimetric (7.6 wt % H₂) and volumetric (110 g H₂/l) capacity combined with low cost, low density and environmental

acceptance [3–5]. Unfortunately, the practical uses of this hydride are prevented by its high stability (the dissociation enthalpy is 74.5 kJ/mol [6]), high decomposition temperature (>573 K at H₂ pressure = 1 bar), and sluggish dehydrogenation kinetics at temperatures below 623 K [4,7,8].

In the past decade considerable progress has been made in the development of powder processing techniques for accelerating the hydride decomposition kinetics. These techniques involve high-energy ball milling and incorporation of different

* Corresponding author. Tel./Fax: +39 0382 987670.

E-mail address: chiara.milanese@unipv.it (C. Milanese).

additives and catalysts. As part of this research, several metals [9–18], metal oxides [19–24], and metallic compounds [25,26] have been tested. Among the metals studied, nickel has attracted considerable attention due to its properties that render it both as an effective catalyst in Mg/MgH₂ sorption reactions and as a destabilizing agent for promoting MgH₂ dissociation [9,12–14,18,23,27–29]. It has also been shown that Ni-doped materials possess excellent cyclic stability [12].

Apart from metallic alloying, some non-metallic elements such as graphitic carbon and carbon nanotubes are known to function as very good anti-sticking agents towards Mg powders (the high ductility of magnesium impedes its high-degree of dispersion during milling). These non-metallic substances also act as efficient catalysts in H₂ sorption reactions [30–36]. Moreover, graphitic carbon facilitates the activation process of Mg-based systems due to its reducing character, that inhibits the formation of new oxide layers on the powder surface following first exposure to hydrogen [30,35].

Up to now only a few papers have been devoted to the study of Mg–Ni–C (graphite) ternary systems [30,31,37–39]. The majority of these studies looked at the effect of adding C to mixtures with Mg₂Ni stoichiometry (Mg 45 wt %–Ni 55 wt %). Only one cited study focused on mixtures containing a Mg stoichiometric excess with respect to the composition of the intermetallic compound [39].

In this work, the effect of increasing the proportion of graphitic carbon from 5 wt % to 15 wt % (in 5 wt % steps) on the reactivity, the activation behaviour and the H₂ storage performance of Mg 85 wt %–Ni 15 wt % mixtures (samples containing “free Mg”) ball milled for only 2 h has been thoroughly investigated. A variety of techniques was used to perform the analyses, including X-ray powder diffraction (XRPD), manometric and coupled manometric–calorimetric measurements, thermal programmed desorption (TPD) runs, and pressure–composition isothermal (PCI) analyses.

The Mg 85 wt %–Ni 15 wt % ratio was selected as the best performer based on results from a thorough exploration of a wide range of binary compositions (Ni content varied between 5 wt % and 55 wt %). An optimal milling time of 2 h was furthermore determined based on comprehensive characterization of mixtures processed for different times (2 h, 4 h, 6 h, 8 h, 16 h). In particular, milling for times longer than 2 h had a detrimental effect on the sorption kinetics of the C-doped samples.

2. Experimental

2.1. Materials

Binary Mg 85 wt %–Ni 15 wt % mixtures and ternary Mg–Ni–C samples with a Mg 85 wt %–Ni 15 wt % fixed ratio and C contents of 5 wt %, 10 wt %, and 15 wt %, respectively, were prepared starting from commercially available Mg (Pometon S.p.a, purity 99.5%, particle size in the range 45 μm–250 μm), Ni (Inco Ltd, purity 99.5%, particles size between 45 μm and 150 μm), and C (Merck, high purity grade hexagonal graphite, particle size less than 50 μm) powders.

2.2. Methods

2.2.1. Samples preparation by ball milling

The as prepared mixtures were processed by MBN Nano-materialia S.p.a (Vascon di Carbonera, Italy) through high-energy ball milling (BM). Only one batch, consisting of approximately 100 g of powder, was produced for each composition studied. The powders were milled in stainless steel bowls (with low carbon content) under 5 bar Ar for $t_{BM} = 2$ h and with a 10:1 ball to powder weight ratio. The processed mixtures were discharged and sent to the Pavia laboratory in ad hoc developed stainless steel containers under an Ar atmosphere in order to prevent any oxidative reaction. Subsequently, the powders were stored and handled in a glove box (Unilab MBraun, Germany) filled with purified and dry Ar (O₂ and humidity contents lower than 0.1 ppm).

2.2.2. Samples characterization

2.2.2.1. Sorption kinetic measurements. The kinetic profiles and the pressure–composition isotherm curves (PCI) were acquired using a fully automated manometric Sievert type apparatus (PCTPro-2000, Hy-Energy & Setaram, pressure measurement accuracy: 1% of reading). The measurements were performed on approximately 0.5 g of the “as milled” mixtures. Details describing the loading of the samples and the calibration of the instrument at the working temperatures were previously reported [40].

First of all, the samples were subjected to 15 consecutive charging (4 h)/discharging (2 h) cycles at 623 K and a starting hydrogen pressure $P_{H_2} = 40$ bar/0.9 bar.

Subsequently, they were re-charged at $P_{H_2} = 40$ bar and 623 K and then cooled down to 473 K at a rate of 10 K/min under isobaric conditions. The samples then underwent a thermal programmed desorption (TPD) run at $P_{H_2} = 0.9$ bar by heating them up to 623 K at a rate of 2 K/min. Finally, they were subjected to isothermal charging/discharging runs at $P_{H_2} = 40$ bar/0.9 bar and at two temperatures: $T = 573$ K (the minimum temperature needed for full desorption) and $T = 593$ K respectively, to study the influence of the working temperature on the sorption performance.

2.2.2.2. Kinetic data analysis. All the data reported in the text and in the Tables concerning both the H₂ intake $H_{2,tot}$ and the rate of the sorption processes were obtained as the average of three independent measurements. In particular, the absorption/desorption kinetics were evaluated as $v_{A,n}/v_{D,n}$, i.e., the average rate (wt % H₂/s) shown by the fully discharged/charged samples upon absorption/desorption of a H₂ content of n wt % (with $n = 3, 5$ and 6). The maximum difference in $H_{2,tot}$ between two different trials conducted at identical temperatures, pressures, and cycle numbers was ± 0.1 wt %, while the differences in the sorption rates between the trials were on the order of 3%.

The desorption kinetic curves recorded at $T = 573$ K, 593 K, and 623 K were fitted (by using SigmaPlot 2000 for Windows, Version 6.0, Regression Wizard utility, number of iterations: 100; step size: 100; tolerance: $1 \cdot 10^{-4}$) according to the Avrami–Erofeev equation [41–43]:

Download English Version:

<https://daneshyari.com/en/article/1273522>

Download Persian Version:

<https://daneshyari.com/article/1273522>

[Daneshyari.com](https://daneshyari.com)