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Hydriding kinetics and process parameters in reactive milling

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Abstract

We focus on the hydriding kinetics of Mg_2Ni/Ni nanocrystalline and $Zr_{55}Cu_{30}Al_{10}Ni_5$ amorphous powders under reactive milling conditions. A methodological approach, based on mechanochemical parameters, is presented to quantify the different behaviour shown by the two systems. A decelerating course characterized the H_2 absorption rate in the Mg based powders. Although they were able to absorb H_2 under static conditions, a speeding up of the kinetics was observed under milling. The mechanochemical gain, g_m, that is the rate increase at the milling outset, was found to depend on the specific milling intensity I_M. By contrast an incubation period preceded the absorption in the case of the Zr based amorphous powders. Furthermore, S-shaped trends described the reactive behaviour in this case even if the kinetics was still dependent on I_M. Irrespective of the milling intensity it was found that the same mechanical work, that is the energy dose, was required to reach the maximum hydriding rate.

Keywords: High-energy ball milling; Gas–solid reactions; Hydrogen storage materials; Mechanochemical synthesis; Nanostructures

1. Introduction

In the development of metal hydrides for energy storage, important results have been reached in the last decade by refining and controlling the microstructure of absorbing phases [1–5]. To this ball milling techniques have been largely employed under inert atmosphere. Hydrogen kinetics and related absorption properties are usually studied under conventional thermal conditions or via electrochemical activation [6–8]. While milling under H_2 atmosphere has been the subject of an increasing number of phenomenological and qualitative works, conversely, in this paper, we related the milling dynamics to chemical conversion data, to quantify possible advantages of absorption under dynamic reactive milling. It allows one to evaluate the amount of H_2 absorbed as a direct consequence of the mechanical energy pulses.

Different characteristic behaviours emerged, which were exemplified by two well known hydrogen storage systems [9,10], Mg_2Ni/Ni composites and Zr-based quaternary alloys. While nanostructured Mg_2Ni/Ni alloy was able to absorb H_2 even under conventional thermodynamic conditions, a period of milling was always needed to activate the process in the case of multicomponent Zr alloys.

2. Experimental

Elemental powders, 3N purity at least, were purchased from different commercial sources. Powder handling, vial charging and sampling were performed inside an inert atmosphere glove box, with O_2 and H_2O content at ppm level. Mg_2Ni:Ni, 94:6 nanocomposites and $Zr_{55}Cu_{30}Al_{10}Ni_5$ amorphous alloys were mechanically alloyed starting from the pure elements. Ball milling processes were performed by a Spex Mixer Mill, Mod. 8000, using hardened steel vials and balls. In particular, the hydriding tests were conducted in an expressly manufactured steel cylinder with covers equipped with gas inlet valves and filters. A powder mass of 8 g was treated in each run. Teflon pipes were used for the vial connection to a volumetric apparatus. Isobar conditions were kept constant inside the vial at 0.4 MPa by a pressure regulator, and absorption was monitored by registering the pressure drop in the gas reservoir.

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Structural analysis was performed using a Rigaku DMax diffractometer equipped with Cu Kα radiation. Crystallite size and strain were evaluated by the Rietveld method employing M.A.U.D. software [11].

Since the ball to powder ratio is of little concern to qualify the milling conditions, then we related the absorption data, expressed as mole $g^{-1}\,s^{-1}$, to the mechanical energy delivered to the powders. Such procedure demands a precise control of the milling dynamics, from which two important parameters can be worked out, that is the impact energy E (J), and the impact frequency N (s^{-1}). Together they define the milling intensity I (W), as $I = EN$, and its normalised value I_M (by scaling I to the powder mass in the vial), which determines the total mechanical work done on the system in the course of the treatment. In the following the values of I_M are quoted for each of the trials. Complete details of the above procedure to characterize the key parameters of the mechanical treatments, as well as of the volumetric apparatus developed to carry out the hydriding processes under milling, are reported in the references [9,12,13].

3. Results and discussion

The X-ray diffraction pattern of the nanocomposite Mg_2Ni/Ni is shown in the lowest trace of Fig. 1. Such sample was able to absorb hydrogen at 298 K without mechanical activation, i.e. without milling, and the relevant kinetic curve, under this static condition, is shown in the Fig. 2, initial curve trend. We plotted the fraction of the total absorbed H_2 moles, α, and the amount of absorbed moles per mass unit, versus the absorbing time. The absorption rate was maximum at the process onset, 3.6×10^{-5} mole $g^{-1}\,s^{-1}$, and decreased throughout, towards a saturation level, at 2.6×10^{-7} mole $g^{-1}\,s^{-1}$, after about 1 h. Such a decelerating behaviour, has been observed for several nanostructured substrates under different thermodynamic conditions [1,3–5]. It could be of general

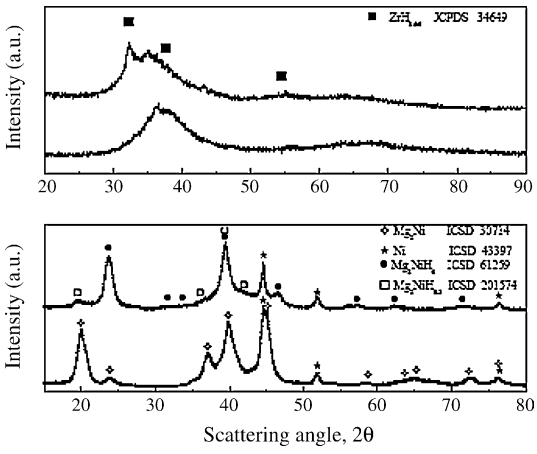

Fig. 1. Cu Kα XRD patterns relevant to Mg_2Ni/Ni (lower curves) and $Zr_{55}Cu_{30}Al_{10}Ni_5$ (upper traces) powders in the as prepared state and after hydriding tests.

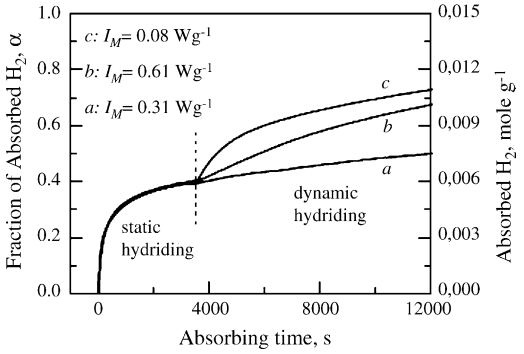

Fig. 2. Hydriding process for the Mg_2Ni/Ni nanocomposite: absorption under conventional thermal activation, left side, was followed by trials carried out under milling conditions at the quoted I_M values.

concern, then, to relate this kinetics to the microstructural features of the nanocomposite here studied. Complete results of the X-ray analyses of the lowest pattern quoted in Fig. 1, are given in a companion paper [13]. Small particles of pure Ni, of about 200 Å inside, corresponding to a surface area of 19 $m^2\,g^{-1}$, were present in the tested powders, coexisting with a spread of Mg_2Ni domains, averaging 60 Å. Beyond the exact value of the crystallite sizes, we underline the coexistence of pure Ni and Mg_2Ni nanostructured domains. From it an interconnected structure can be surmised, with privileged diffusion path for H_2. It can be conceived that the Ni patches play a key role in the dissociative chemisorbing of H_2 molecule, which is maintained as the first step of H_2–solid interaction, with consequent spill-over towards the absorbing Mg_2Ni phase and final bulk diffusion. The initial lack of product phases surrounding the Mg_2Ni grains justifies the initial high rate. Then, as absorption proceeded, a longer diffusion path is demanded for the hydrogen atoms. Furthermore, the hydride layer formation reduces progressively the developing hydride-residual Mg_2Ni interlayer, and consequently the number of available absorbing sites. According to the contracting core model [14], it explains the decreasing of the rate until saturation.

With the aim to verify the role of the mechanical action on the absorbing behaviour, hydriding was continued under milling, as shown in Fig. 2, where new rising trends were registered following the outset of the mill. Three different intensities were tested, and the differences between the initial absorbing rates under milling and the limit rate under static conditions, provide a first evaluation of the milling action. The absorbing rate increased to 3.6×10^{-7} mole $g^{-1}\,s^{-1}$, 7.58×10^{-7} mole $g^{-1}\,s^{-1}$, and 1.7×10^{-6} mole $g^{-1}\,s^{-1}$, respectively, at 0.31 W g^{-1} (a), 0.61 W g^{-1} (b), and 0.88 W g^{-1} (c). Referring these quantities to 2.6×10^{-7} mole $g^{-1}\,s^{-1}$ quoted above for the process going to static saturation, one obtains a quantitative evaluation of the reaction speeding up: we called it mechanochemical gain, g_m. In detail $g_m = 1.0 \times 10^{-7}$ mole $g^{-1}\,s^{-1}$ at $I_M = 0.31$ W g^{-1}, $g_m = 4.98 \times 10^{-7}$ mole $g^{-1}\,s^{-1}$ at 0.61 W g^{-1}, and $g_m = 1.44 \times 10^{-6}$ mole $g^{-1}\,s^{-1}$ at 0.88 W g^{-1}. Absorption quantitative