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.
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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
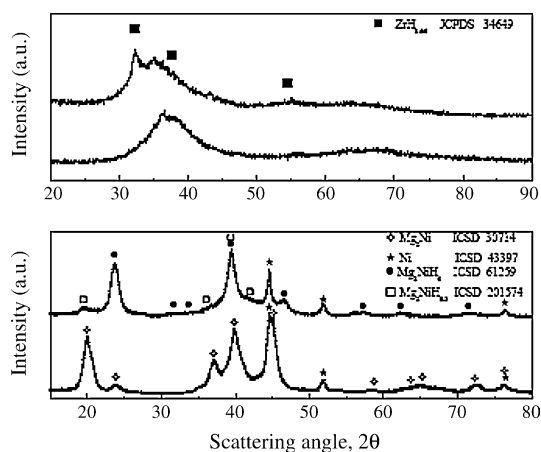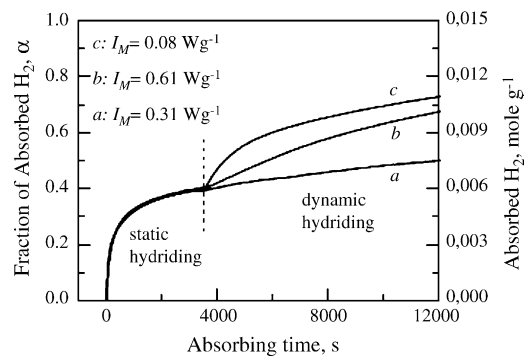

Fig. 2. Hydriding process for the Mg_2Ni/Ni nanocomposite: absorption under conventional thermal activation, left side, was followed by trials carried out under milling conditions at the quoted I_M values.

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 m² 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

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.

data can be scaled to a microscopic view: the above g_m values, expressed as atoms s^{-1}, are respectively 1.2×10^{17}, 5.99×10^{17} and 1.74×10^{18}, which, in turn, when related to the collision frequency (in these tests a milling regime of 29 collisions per second was employed) permit to estimate the number of atoms chemisorbed as a result of the kinetic energy transferred during a collision, corresponding to 4.15×10^{15} atoms hit^{-1}, 2.07×10^{16} atoms hit^{-1}, and 5.98×10^{16} atoms hit^{-1}, respectively. It is noticeable that even for a small augment of I_M, g_m increased more than 14 times. Since in the g_m parameter several factors combine, a deeper understanding of the reaction mechanism requires further considerations and some work is in progress on this topic. We conclude this part on Mg$_2$Ni/Ni alloy by noticing that at the end of mechanical treatment, i.e. when no more hydrogen absorption was observed, the same structural transformation occurred in the three specimens, independently by the applied I_M. Representative pattern is shown in Fig. 1. The main phase is the Mg$_2$NiH$_4$, accompanied by the poorer hydride Mg$_2$NiH$_{0.3}$, and their relative amount justify the final H/M wt% of 3.02, while the percentage of Ni did not change. Preliminary tests relevant to crystalline Zr evidenced that at room temperature and 0.4 MPa of H$_2$, absorption started only after a milling period, related to the milling intensity, and an S-shaped kinetics was observed, see the inset in Fig. 3. Amorphous powders of the Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{10}$ composition showed a similar behaviour. Absorption started only under dynamic regimes and after an incubation period, and still sigmoid kinetic curves were registered. However, a strong dependence was observed by modulating the milling intensity. Results are presented in Fig. 3 as α versus the milling time. The value $\alpha = 1$ corresponds, in all the tests, to 1.45 H/M wt%. The working I_M are given in the figure caption. Such shape of kinetic curve has been already reported for mechanochemical reaction between solids [12] or solid and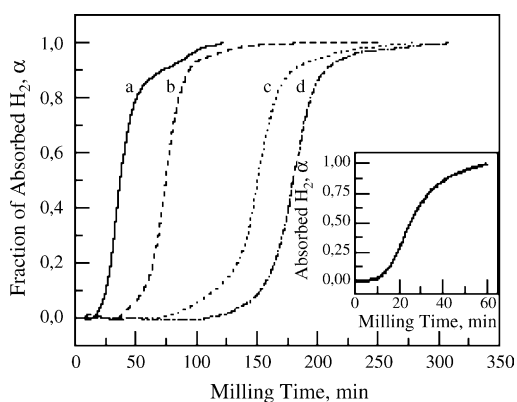 gas phases [15,16]. While the incubation period has been often related to the presence of oxide layers, which hinder the start of the absorbing reaction, the accelerating trend has been explained in terms of nucleation and growth mechanism referring to a JMAK kinetics [16,17]. As a matter of fact it is possible to fit the experimental sigmoids by one of the equations related to nucleation and growth phenomena, however it is not straightforward to ascribe a direct physical meaning to the parameters worked out since the separate nature of the reactants in powder form, which displays a distribution of the particle dimensions, and subjected to thermal shocks and mechanical pulses [14]. In these trials, due to the lack of absorption under static regimes, the g_m corresponds to the hydriding rate originating as a consequence of mechanically induced regimes, and an analysis in terms of g_m is still possible. However, a different approach was followed here to highlight the effect of I_M on the absorbing rate.

We considered the time, t_{MAX}, at which the curves in Fig. 3 reached the maximum transformation rate. Then a linear trend is observed by quoting $1/t_{MAX}$ versus I_M for the tested samples, as shown in Fig. 4. It is then possible to compare the experimental results according to the:

$$\frac{1}{t_{MAX}} = KI_M$$

where K is the slope of the linear trend. It is equivalent to write:

$$K' = \frac{1}{K} = I_M t_{MAX} = \text{constant}$$

where $K' = 493\,\text{J g}^{-1}$ is a constant, and represents the specific energy dose, D_M, which must be delivered to the powders to reach the maximum absorption rate. One also notes that D_M does not depend on the rate of the energy transfer, I_M, and therefore is an invariant quantity, which characterises the process. Such behaviour suggests that the same hydriding mechanism is operative, independently by the applied I_M, as it is also confirmed by the same structural evolution which
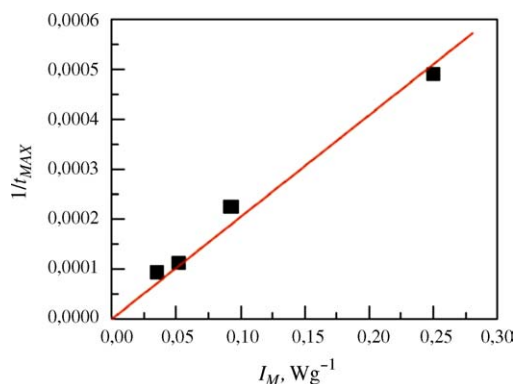

Fig. 3. Absorption kinetic curves for the Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_5$ amorphous powders at different milling regimes. All the traces show an evident sigmoid trend with induction milling periods depending on the applied I_M. Curve a: $I_M = 0.25\,\text{W g}^{-1}$; curve b: $I_M = 0.09\,\text{W g}^{-1}$; curve c: $I_M = 0.05\,\text{W g}^{-1}$; curve d: $I_M = 0.03\,\text{W g}^{-1}$. In the inset kinetic trend relevant to pure crystalline Zr is shown.

Fig. 4. H$_2$ absorption in Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_5$ system. Linear trend in the plot of the reciprocal values of the time corresponding to the maximum absorption rate, $1/t_{MAX}$, versus the specific milling intensity I_M.

followed the absorption: in all the tests the separation of crystalline $ZrH_{1.66}$ accompanied the formation of the amorphous hydride, see the highest trace in Fig. 1 and the reference [10].

4. Conclusions

The different behaviour of Mg and Zr based systems in the kinetics of hydrogen absorption under mechanical treatment is presented. Continuously decreasing and s-shaped kinetics are typical of heterogeneous reactions in solid state chemistry, and experimental data can be fitted by known equations. To gain qualified insights from the resulting fitted parameters, as in the case of established, thermally activated, reaction mechanisms is, however, a difficult task due to the specificity of hydrogen absorption under milling. Quantitative evaluation and control of specific mechanochemical parameters, as for example, g_m and D_M is possible according to the presented procedure. If this methodology could offer new opportunities for an alternative kinetic approach, and to highlight new aspects of the hydriding properties under milling is, at present, under confirm.

Acknowledgements

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