

Methodological Aspects in the Study of Mechanochemical Processes

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Abstract

A methodological approach is presented to study gas-solid interactions under mechanochemical activation. Based on a detailed analysis of bulk microstructure, surface features control of milling energy parameters, the H₂ sorption kinetics in Mg₂Ni/Ni nanostructured powders was studied. Hydriding rate and specific parameters such as turnover frequency, mechanochemical gain and instantaneous yield were used to analyze the process on an absolute scale, to elucidate the reaction mechanism and highlight mechanochemical effects.

INTRODUCTION

While mechanical activation attracts wide attention for the synthesis of a variety of metastable systems, most of the studies in this field are phenomenological. The understanding of the complex physicochemical phenomena occurring under a mechanical action is still unsatisfactory, a detailed analysis of the several features involved being required [1–5]. Bulk properties and microstructural evolution should be considered together with active surface qualities and both of them need to be related to the transferred mechanical energy [6]. This topic has been already dealt with for solid homogeneous systems [7, 8]. This contribution describes a methodology aimed at both quantifying the mechanochemical aspects and expressing the reaction kinetics in heterogeneous systems in terms of turnover frequency [9]. In particular, the H₂ absorption in a nanostructured composite Mg₂Ni/Ni system was studied.

A large number of literature data provides indeed a suitable reference framework [10, 11]. Here, the metallic Ni in excess at the surface of the system has a known catalytic role in the activation of H₂ molecules.

METHODOLOGICAL APPROACH AND EXPERIMENTAL PROCEDURES

The complexity of mechanically activated gas-solid interactions over nanostructures requires a detailed analysis of interrelated factors such as surface chemistry, microstructure, strain content and texture and milling dynamics. Surface chemistry underlies any absorption process preceding either the spillover phenomena or the dissolution into the bulk. Chemisorption depends on the number, nature and activation energy of adsorption sites, on the sticking coefficient and finally on the surface coverage. It is then specific for adsorbed molecules and substrates. However, a neat correlation exists between nature and number of activation sites and microstructure of the substrate. The average dimension of the coherent domains defines indeed the percentage of surface atoms exposed, *i.e.* the dispersion ruling the population of surface active sites. The total accessible surface area of the active phase can be estimated by resorting to a geometrical evaluation for each specific adsorbing metal. Surface concentration values can be thus derived and expressed as number of surface atoms per unit area (n_s) [12].

Conversely, the evaluation of the absolute number of surface atoms, N_s , requires the quantification of the specific surface area

$$S_{sp} = \frac{6 \cdot 10^4}{\langle L \rangle} \text{ (m}^2/\text{g)},$$

where the average crystallite size $\langle L \rangle$ is obtained from X-ray diffraction analysis. Then,

$$N_s \text{ [atoms]} = n_s S_{sp} m_p \text{ [atoms/m}^2\text{]} [\text{m}^2/\text{g}][\text{g}]$$

where m_p is the batch mass. The above quantities can be related to mechanochemical reaction kinetics by resorting to some parameters used in heterogeneous catalysis. The conversion

$$\text{rate } r \text{ can be expressed as either } r = \frac{dn_{mol}}{dt} \text{ (mol/s)}$$

$$\text{or } r_s = \frac{dn_{mol}}{m_p dt} \text{ [mol/(g s)]}$$

indicating how many moles are transformed per gram of mass batch in one second. Finally, the Turnover Frequency

$$\text{TF} = \frac{dn_{mol}}{m_p S_{sp} n_s dt} \text{ [mol/(at. s)]}$$

expresses instead the number of reactive events occurring in one second per active site. It permits then the definition of the solid reactivity on an absolute scale. TF should not depend indeed on the dispersion of the active phase and should be an invariant quantity for a given reaction carried out at constant pressure and temperature.

The previous considerations can be applied to mechanochemical processes provided that the milling parameters are properly defined and controlled. The mechanical treatment intensity affects indeed the structural and electronic behaviour of both bulk and surfaces, also governing eventual diffusion processes. Our experimental methodologies, detailed in previous works [8], apply to ball mills provided that a single ball is employed, the vial motion is analytically described and quasi-inelastic collisions occur. Under such circumstances, the average impact energy E (J/hit) and the collision frequency N (hit/s) can be determined. A specific milling intensity $I_M = NE/m_p$ (W/g) can be thus defined, which represents the rate of mechanical energy transfer to powders. The total work done on the system in the time t is therefore represented by the energy dose $D_M = I_M t$ (J/g). The average mechanochemical yield Y (mol/kJ) is finally obtained by scaling r to I_M [8]. Taking

advantage of such quantities, the Mechanochemical Turnover Frequency

$$\text{MTF [mol/(at. hit)]} = \frac{r}{m_{p,i}^{hit} S_{sp,i} n_{s,i}} \frac{1}{N}$$

can be defined, where $m_{p,i}^{hit}$ is the mass fraction cold-worked at impact. MTF expresses the number of molecules transformed at each impact per surface atom of the active phase. Scaling MTF to the impact energy provides

$$\text{MT}_E \text{ [mol/(at. J)]} = \frac{r}{m_{p,i}^{hit} S_{sp,i} n_{s,i}} \frac{1}{N} \frac{1}{E}$$

i.e. the instantaneous yield per surface atom of the active phase. Finally, the mechanochemical gain $g_m = r_{dyn} - r_{st}$ can be introduced to compare mechanically and thermally activated processes and express the excess molecules absorbed per hit.

Hydriding runs were followed either under static conditions or under reactive milling. The absorption process was also started under static conditions and continued under milling up to complete saturation.

The detailed experimental set-up employed in the absorption test was reported in previous works [6]. Crystalline Mg_2Ni powders with a 6 mass % excess of metallic Ni were prepared by mechanically activated self-sustaining high temperature synthesis, and refined under different, and controlled, grinding conditions, by using different mills. Together with these samples, in the following described as A1 and A2, we prepared an additional A3 crystalline specimen, and the pattern was completed by a sample synthesized by mechanical alloying of the pure elements, in the following B.

RESULTS AND DISCUSSION

The microstructural parameters resulting from the XRD analyses of the prepared samples are quoted in Table 1. A comparison of the data relevant to samples B, A1 and A2 reveals that the average crystallite size of Ni and Mg_2Ni phases was around 10–20 nm. Generally, significant structural differences in the hydrided samples also emerge. Characteristic trends of absorption under static conditions are presented in Fig. 1. All the samples display a deceleratory kinetics, *i.e.* the absorption rates

TABLE I

Sample, phase content and microstructure parameters

Sample	Phases	mass %	$\langle D \rangle$, nm	Strain, %	S_{sp}^* , m ² /g	Conversion rate**, mol/(g s)
SHS						
A ^a	Mg ₂ Ni	89.5	40.4	$3.0 \cdot 10^{-5}$	18.1	
	Mg	2.7	30.0	$8.0 \cdot 10^{-3}$	57.5	
	Ni	6.8	30.9	$8.4 \cdot 10^{-3}$	10.9	
	MgO	1.0, traces	–	–	–	
	MgNi ₂					
A1 ^b	Mg ₂ Ni	91.0	6.2	$1.5 \cdot 10^{-4}$	117.7	$2.05 \cdot 10^{-4}$
	Mg	1.0	12.3	$3.1 \cdot 10^{-2}$	140.2	
	Ni	5.0	20.8	$2.4 \cdot 10^{-4}$	16.2	
	MgO	3.0	–	–	–	
A2 ^c	Mg ₂ Ni	92.0	3.7	$2.7 \cdot 10^{-4}$	197.3	$1.95 \cdot 10^{-3}$
	Ni	3.0	10.0	$1.1 \cdot 10^{-2}$	33.8	
	MgO	5.0	–	–	–	
MA						
B	Mg ₂ Ni	94.0	6.0	$6.0 \cdot 10^{-3}$	122	$3.6 \cdot 10^{-5}$
	Mg	–	–	–	–	
	Ni	6.0	20.0	$2.0 \cdot 10^{-3}$	16.9	

^aCrystalline as-prepared sample. ^bRefined by impact energy. ^cRefined by shearing energy.

*Specific surface area calculated according to $S_{sp} = 3 \cdot 10^4 / (\rho \langle D \rangle)$, with ρ bulk density.

** At the onset of the static absorption.

progressively decrease during the course of the reaction. Such a behaviour, already observed in heterogeneous reactions [13], has been related *i*) to the hydride layer growing on the external surface of the Mg₂Ni, which must be crossed throughout for further growth; and *ii*) according to the contracting core model, to

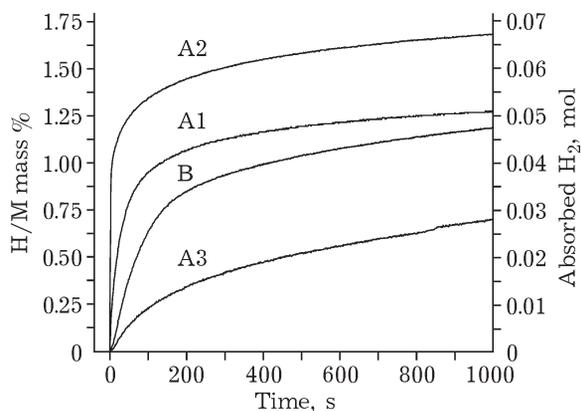


Fig. 1. Hydrogen absorbing kinetics for the nanosized A1, A2, A3 and B samples characterized in Table 1. Irrespective to preparation mode the hydriding process is deceleratory throughout.

a progressive reduction of the inner area at the interphase between developing hydride phases and the intermetallic compound [13].

Conversion rates are reported in the last column of Table 1. Nanostructured samples showed hydriding rates higher than the A3 one, also absorbing a larger amount of hydrogen. Moreover, A2 showed the highest value, two orders higher than the one recorded for the mechanically alloyed B sample, in spite of the smaller Ni content. Structural features give a possible explanation. The dimensions of the Ni domains in the A2 sample, about 10 nm, are smaller than those in the remaining A1 and B samples, about 20 nm. The fastest A2 kinetics relates well to these reduced dimensions and therefore to the larger surface area of the Ni particles. The most probable explanation for the faster kinetics of the A2 sample lies however in the average size of the Mg₂Ni particles, about 3.7 nm, which are half-sized the ones of both A1 and B samples.

The small size of bulk Mg₂Ni determines a reduced diffusion path for hydrogen atoms and,

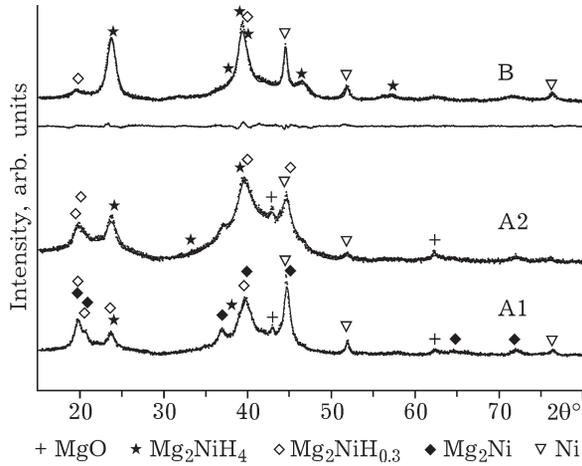


Fig. 2. XRD patterns of the $\text{Mg}_2\text{Ni}/\text{Ni}$ samples after the first hydriding run. Irrespective to the sample preparation techniques, $\text{Mg}_2\text{NiH}_{0.3}$ and traces of monoclinic hydrogen-rich Mg_2NiH_4 result in the samples subjected to static hydriding runs – lower patterns. In the upper pattern, which refers to a B-type sample charged by reactive milling, the hydrogen-rich Mg_2NiH_4 is the prevailing hydride phase.

together with the higher surface area of Ni, promotes the overall absorbing kinetics of A2. The larger strain content of the Mg_2Ni host lattice of the mechanically alloyed sample ($6.0 \cdot 10^{-3}$), nearly two orders of magnitude larger than in A1, is probably another cause of the B slower kinetics. Such results confirm the important role of microstructural features and indicate that the structural disorder plays an opposite role on the surface and bulk phases.

The XRD patterns of the hydrogenated powders shown in Fig. 2 support the previous considerations. The $\text{Mg}_2\text{NiH}_{0.3}$ hydrogen-poor phase dominates the A1 and A2 patterns. This suggests that the high strain of the nanostructured material decreases at least partially the absorption capacity under static conditions. Conversely, the pattern relative to B-type powders hydrogenated under milling in the same Figure is characterized by the hydrogen-rich Mg_2NiH_4 hydride.

In the following, the paper focuses on the sorption experiments under milling conditions on B-type specimens. Representative kinetic curves are plotted in Fig. 3. Milling started after 1 h of absorption under static conditions (curve 1). Such a curve is compared to the one obtained under dynamic conditions since the onset of the process (curve 2). While the asymptotic trends of both the curves suggest sim-

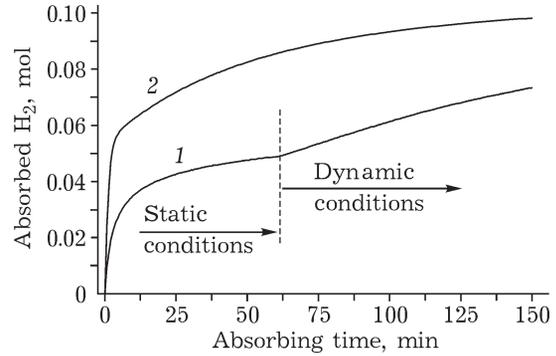


Fig. 3. Absorbed hydrogen moles for $\text{Mg}_2\text{Ni}/\text{Ni}$ powder samples as a function of the elapsed time: 1 – collected under static absorbing conditions up to the marker, then under milling; 2 – the process carried out under milling from the beginning. $I_M = 0.68 \text{ W/g}$.

ilar mechanistic features, specific mechanochemical effects can be inferred by relating the absorption rates to microstructure and milling dynamics.

Hydriding under milling starts with a rate, r_{dyn} , of $8.2 \cdot 10^{-5} \text{ mol}/(\text{g} \cdot \text{s})$ (corresponding to $6.6 \cdot 10^{-4} \text{ mol/s}$ since a batch of 8 g was employed), whereas $3.6 \cdot 10^{-5} \text{ mol}/(\text{g} \cdot \text{s})$ ($2.9 \cdot 10^{-4} \text{ mol/s}$) is the absorption rate, r_{st} , recorded at the beginning of the static run. Such an increase is exclusively due to the mechanical action, and a mechanochemical gain $g_m = 3.7 \cdot 10^{-4} \text{ mol/s}$ is found. This quantity is equivalent to $4.4 \cdot 10^{20} \text{ at./s}$ of hydrogen absorbed and corresponds to an atomic gain per hit, g_{at} , of $1.5 \cdot 10^{19}$ atoms per hit, given an impact frequency of 29 s^{-1} . The activation of these hydrogen molecules is due to the powder fraction cold-worked at each impact and to the pertinent Ni fraction. To pursue this relationship somewhat further, we consider a mass entrapped at each collision of about $1 \cdot 10^{-4} \text{ g}$ [8]. Since the initial Ni fraction is about 6.0 mass % of the powder batch, about $6 \cdot 10^{-6} \text{ g}$ of Ni are involved in each impact. Taking into account the specific surface area of Ni ($16.9 \text{ m}^2/\text{g}$), the total activated Ni area in the strained powders is roughly $1.0 \cdot 10^{-4} \text{ m}^2$. This area involves $1.6 \cdot 10^{15}$ surface Ni atoms, according to the surface atomic density quoted in the literature for polycrystalline Ni ($1.54 \cdot 10^{19} \text{ at./m}^2$) [12].

When the excess of absorbed hydrogen atoms g_{at} given above ($1.5 \cdot 10^{19}$ atoms per hit) is related to the surface Ni atoms involved in the collision event ($1.6 \cdot 10^{15}$), it appears that the Ni

landing areas in the impacted mass reach an excited state able to create a large number of chemisorbed molecules. Considering that $1.4 \cdot 10^{17}$ atoms are located at the Mg_2Ni free surface (we are still considering the impacted powder fraction), it also appears that the excess quantity of activated hydrogen atoms dissolves into the grain boundaries or crosses the Mg_2Ni interface areas without diffusion constraints.

The mechanical treatment speeds up the hydriding reaction even at the saturation stage of the static run, as shown from curve 1 in Fig. 3. According to the curve slopes, the observed rate at the ultimate limit of the static absorption, $2.6 \cdot 10^{-7} \text{ mol}/(\text{g} \cdot \text{s})$, increases to $4.4 \cdot 10^{-7} \text{ mol}/(\text{g} \cdot \text{s})$ at the milling outset with a mechanochemical gain of about $5.5 \cdot 10^{16}$ atoms per hit. The mechanical action creates new inter-phase boundaries in the whole impacted mass, making the residual hydrogen-free core of the Mg_2Ni particles more accessible for hydrogen dissolution. Further interesting considerations emerge when the results are approached from a mechanochemical point of view. Relating the r_{dyn} values, measured at the onset of the process and at the static saturation level, to the surface Ni atoms involved in the collision event, the MTF values can be obtained. Their values are equal to about $1.8 \cdot 10^4$ and 100 H_2 atoms per surface Ni atom at each impact, respectively, at the initial stage of the process and after the starting of the milling action. Considering that MTF should be an invariant of the hydriding process, the strong decrease of about four orders of magnitude seems to indicate a different role of surface activity, suggesting a mechanistic change from a surface- to a bulk-controlled kinetics.

Similar inferences can be gained evaluating the instantaneous mechanochemical yield of the hydriding process, defined as (r_{dyn}/I_M) , which drops from 0.2 to $9.1 \cdot 10^{-4} \text{ mol}/\text{kJ}$. These values refer respectively to the beginning of curve 1 and to the onset of milling in curve 2 in Fig. 3. This can be explained by noticing that at the very beginning of the reactive milling process no surface hydride layer hinders the diffusion process. The mechanical work done on the system is mainly spent in the production of surface excited states and in hydrogen activation. Conversely, comminution work is continuously

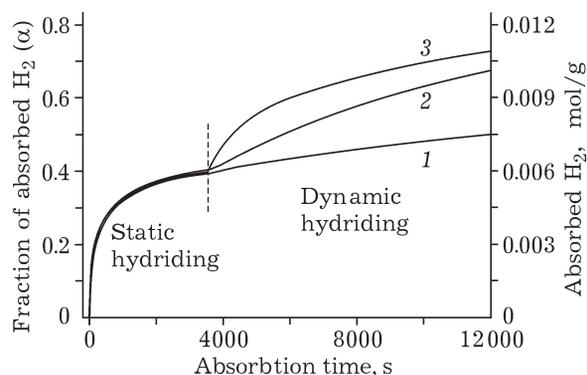


Fig. 4. Hydriding process for the $\text{Mg}_2\text{Ni}/\text{Ni}$ nanocomposite: absorption under conventional thermal activation (left side) was followed by trials carried out under milling conditions at the quoted I_M values, W/g : 0.31 (1), 0.61 (2), 0.88 (3).

required at the advanced stages of the reaction process.

The two-step hydriding process was repeated under similar static conditions, but at increased milling intensity for the dynamic step. Some representative curves are plotted in Fig. 4. Their static sections overlap, whereas they diverge under milling: absorption rates and hydrogen uptake progressively increase with I_M . The resulting values of mechanochemical gain per hit, for several trials, are reported in Fig. 5 as a function of I_M . The ratio increases markedly following apparent exponential behaviour as suggested by the continuous best fitted curve. Within the intensity window investigated here, the mechanochemical gain increases about 25 times for a relatively modest increase of I_M

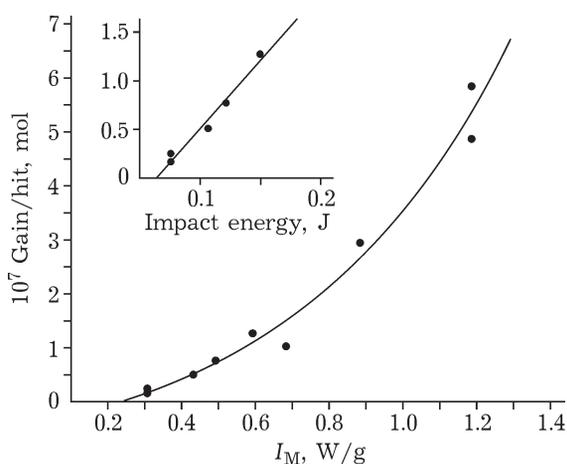


Fig. 5. Increase in the mechanochemical gain per hit (g_m) as a function of the milling intensity (I_M). Inset: mechanochemical gain vs. impact energy for experiments carried out at the same impact frequency.

(from 0.3 to 1.2 W/g). Before concluding we note that such a behavior is a combination of the effects of collision energy and collision frequency. To separate the two contributions, data obtained at the same impact frequency (29 hit/s) are quoted in the inset of the same Figure versus the impact energy. The data course crosses the abscissa energy axis at a positive E value, at about 0.06–0.07 J, suggesting the existence of a mechanochemical energy threshold, below which the mechanical treatment cannot increase the hydriding process kinetics. While the occurrence of an impact energy threshold was already reported for homogeneous mechanochemical reactions [6, 14], however, the present case involving the activation of gaseous molecules needs a deeper investigations.

CONCLUSIONS

The detailed comprehension of the gas-solid interactions under mechanical input requires the determination and the control of relevant key parameters at once. The effort presented in this work moves along this direction, aiming at finding out the rate determining step of the process, and the hydriding reaction mechanism: for this, the continuous control of the kinetic energy transferred to the powders was paralleled by numerical estimation of surface and

bulk atomic density. The evaluation of representative intrinsic parameters, providing local instantaneous views of the macroscopic process, highlighted the occurrence of mechanochemical effects at selected stages of the reaction.

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