

Mechanochemical effects on hydrogen absorption in Mg₂Ni alloys under mechanical processing conditions

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Abstract The present investigation focuses on the kinetics of hydrogen absorption in Mg₂Ni powders subjected to thermal or mechanochemical activation. The process was initially carried out under isobaric-isothermal conditions in a mechanochemical reactor at rest. Once the static hydrogen absorption process approached completion, the system was subjected to mechanical activation at constant hydrogen pressure. The mechanical treatment of powders induced further hydrogen absorption at rates depending on the processing intensity. The observed mechanochemical effect is related to the generation of reactive surfaces when mechanical loads apply on powders. The reactive surface area involved in the mechanochemical hydrogen absorption and the duration of the absorption process are roughly estimated.

Introduction

Mechanochemistry is the branch of Chemistry dedicated to the study of chemical reactions driven by the transfer of mechanical energy [1–3]. The capability of mechanical

forces of triggering chemical processes is intimately connected with the departure of solid phases from thermodynamic equilibrium when the content of structural defects increases [2–5]. The atomic species involved in plastic deformation events develop indeed distorted coordination shells and are therefore characterized by relatively high potential energies, which permit the attainment of unusual states of reactivity [6–11]. These aspects have been exploited more or less consciously since ancient times, but only in the last three decades mechanochemical methods have fully shown their potential with the successful application to the synthesis and processing of advanced materials [12]. The degree of development attained by mechanochemistry is however remarkably lower than by other classical fields of chemistry such as thermochemistry and photochemistry [5, 13]. The gap is particularly evident when comparing the detailed knowledge of mechanistic scenarios for thermally activated chemical reactions in solution phase with the scarce information on the elementary stages of mechanochemical transformations [14]. This is in part due to the complexity of the studies concerning the physics and chemistry of solid phases under shear, which require expensive experimental apparatuses and the establishment of a coherent conceptual framework accounting for coupled thermal and shear effects [5, 8–11]. It however also originates from a largely empiric use of mechanical processing for the chemical activation of powders with no attention to the careful characterization of its fundamental features [12]. Thus, only a generic statement of the relationship between reactivity and defect content is often claimed to justify the unusual chemical behavior of matter subjected to mechanical treatment. It is conversely rare that mechanically activated processes are investigated in depth in the attempt of separating thermal and mechanochemical effects on a quantitative basis [15].

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In this work we demonstrate how simple can be the achievement of such objective in the case of mechanically activated chemical reactions between gaseous phases and solid substrates. Our attention focuses in particular on the absorption of molecular hydrogen over a nanocrystalline Mg_2Ni alloy to form the Mg_2NiH_4 hydride. The choice of investigating such hydrogenation reaction relies upon the fact that chemical strategies for hydrogen storage are currently under intense scrutiny [16] and make large use of mechanical processing methods. Moreover Mg_2Ni hydriding under reactive milling conditions was the subject of previous reports by different authors [17–20]. We therefore hope that this work could attract interest on the finer details of the mechanochemical hydrogenation processes and that the study of different systems could favor a rapid advance of fundamental knowledge.

Experimental methodologies and results

Hydrogen sorption experiments were performed on nanocrystalline $\text{Mg}_2\text{Ni}/\text{Ni}$ -6 wt.% composite powders prepared by mechanical alloying from pure elements. Synthesis details as well as structural characterization of the prepared samples were reported in a previous paper [20]. Preparation stages and handling procedures were carried out under inert argon atmosphere to avoid undesired oxidation reactions. The content of moisture and oxygen was estimated to be <2 ppm.

$\text{Mg}_2\text{Ni}/\text{Ni}$ powders obtained were divided into two amounts of 8 g each. The amounts were separately exposed to the reactive hydrogen atmosphere within a stainless steel cylindrical reactor equipped with gas valves on its bases for gas inlet and pressure control. Powders were introduced into the reactor chamber together with a stainless steel ball. The mechanochemical reactor was then fixed on the mechanical arm of a commercial Spex Mixer/Mill mod 8000. The argon atmosphere within the reactor chamber was then evacuated and replaced by gaseous hydrogen at a pressure of 0.4 MPa [20]. Such pressure value was kept constant and the hydrogen absorption was monitored by evaluating the pressure drop into the hydrogen reservoir connected with the reactor [20].

Absorption was initially performed under static conditions, i.e., with the reactor at rest. This permitted to study the absorption kinetics under conventional isothermal conditions. The rate of hydrogen absorption was seen to regularly decrease according to a smooth trend asymptotically approaching a null value. When the absorption rate reached about two thousandths of its initial value, the static absorption process was considered roughly complete, being any further hydrogen uptake negligible. At that point, the absorption process was interrupted and replaced by a

dynamic one by operating the mill at a frequency of ~ 14.5 Hz. When the mechanical treatment started a net discontinuity in the absorption rate was observed: from approximately null values to finite ones with a net hydrogen uptake. The initial values of the absorption rate under dynamic conditions depended on the intensity I of the mechanical processing, defined as the product between the frequency N of collisions and the average impact energy E [21]. It is here worth remembering that these parameters can be accurately evaluated by means of a suitably developed methodology when a single ball is used together with a powder charge adequate to assure that impacts between ball and reactor walls occur under inelastic conditions [21]. This is the case of the experimental trials carried out for the present investigation, being 8 g of Mg_2Ni sufficient to attain the aforementioned processing conditions. The two 8 g powder amounts were processed at different intensity values, namely 2.48 and 4.88 W, obtained by using stainless steel balls with a mass of ~ 10 and 20 g, respectively [20]. It follows that the average impact energies E amount approximately to 0.084 and 0.168 J [21]. The frequency N of collisions is instead roughly equal to 29 Hz [21].

X-ray diffraction methods were used to monitor any phase transformation induced by the hydrogen absorption process. A Rigaku DMax diffractometer equipped with a $\text{Cu } K_\alpha$ radiation tube and a graphite monochromator in the diffracted beam was used. Analyses were performed on samples of compacted powders. The Brunauer-Emmett-Teller method was employed to estimate the area of the free surfaces of the powders. Adsorption–desorption cycles were carried out with a Sorptomatic 9000 working under nitrogen atmosphere. The specific surface area of initial Mg_2Ni powders was found to amount approximately to $15 \text{ m}^2 \text{ g}^{-1}$.

The experimental results obtained are summarized by the kinetic curves reported in Fig. 1. Such curves relate the total number m of hydrogen moles absorbed under static and dynamic conditions to the time t . The curve portions describing the absorption kinetics under static conditions display an excellent superposition, pointing out a satisfactory reproduction of experimental data. The beginning of dynamic absorption is clearly indicated by the sudden rise of the absorption rate pertaining to the second portion of the kinetic curves. The highest initial absorption rate under dynamic processing conditions pertains to the powders processed at the highest intensity.

The two sets of experimental data clearly show that the mechanical processing is able to induce further uptake of gaseous hydrogen once that the isothermal absorption process has stopped. This can be regarded as a clear example of mechanochemical effects originating from the transfer of mechanical energy to the partially hydrogenated

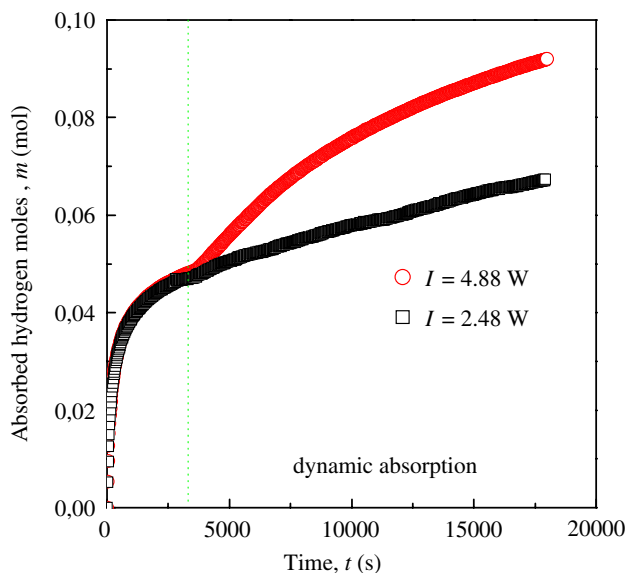


Fig. 1 The number m of hydrogen moles absorbed as a function of time t . The vertical dotted lines mark the boundary between static and dynamic absorption processes. The portions of kinetic curves referring to dynamic absorption are explicitly indicated. Dynamic absorption is carried out at the quoted intensity values

powders. The analysis of the kinetic curves describing the absorption of hydrogen under mechanical treatment and their tentative rationalization in terms of phenomenological quantities will be the focus of the following section.

Kinetics of the hydrogen absorption process under dynamic conditions

According to the experimental data quoted in Fig. 1, the static absorption process is interrupted at a time t_s roughly amounting to 3,540 s when the number m_s of hydrogen moles absorbed is approximately equal to 4.7×10^{-2} mol. Under the assumption that the hydrogen absorbed forms a hydride layer of uniform thickness at the powder particle surface and remembering that the total surface area of powders amounts to about 120 m^2 , the number of hydrogen moles absorbed per surface unit, $m_{s,s}$, is equal to $3.9 \times 10^{-4} \text{ mol m}^{-2}$.

The number of hydrogen moles absorbed under dynamic conditions is equal to $m_d = m - m_s$. The kinetics of dynamic absorption processes can be referred to the scaled time $t_d = t - t_s$. It is however worth noting that referring the kinetics of mechanically driven reactions to the number of collisions $n = Nt_d$ is a more appropriate choice. The absorption process under mechanical processing conditions is satisfactorily described by an exponential curve tending asymptotically to a final value $m_{d,f}$ of hydrogen moles absorbed roughly equal to 5.5×10^{-2} mol for both the experimental data sets. A linear trend is indeed obtained

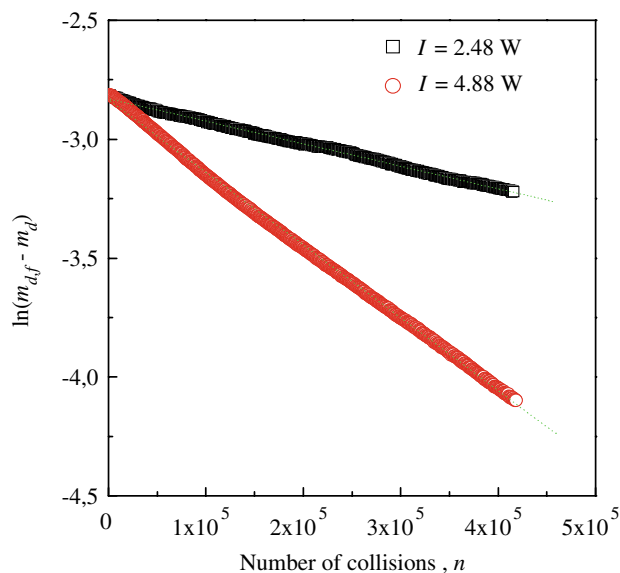


Fig. 2 The Neperian logarithm of the difference between the asymptotic value $m_{d,f}$ and the number m_d of hydrogen moles absorbed under dynamic conditions, $\ln(m_{d,f} - m_d)$, as a function of the number n of collisions. Data arrange according to linear trends. Best-fitted lines are also shown together with the intensity values

when the Neperian logarithm of the difference between the asymptotic value $m_{d,f}$ and the number m_d of hydrogen moles absorbed under dynamic conditions, $\ln(m_{d,f} - m_d)$, is quoted as a function of the number n of collisions. It follows that the kinetic law can be expressed as

$$m_d = m_{d,f}(1 - e^{-kn}), \tag{1}$$

where k is the apparent rate constant for the mechanochemical hydrogen absorption process. The best-fitting of the linear trends reported in Fig. 2 yields rate constant values of 3.1×10^{-5} and 1.1×10^{-4} for the hydrogenation reactions carried out at 2.48 and 4.88 W, respectively. The product kn is therefore very small unless the number n of collisions is very large and its minimum value amounts exactly to k when only a single collision has occurred, i.e., when n is equal to 1. The real physical meaning of the mechanochemical rate constant k can be pointed out by noting that, under such circumstances, $e^{-k} \cong 1 - k$. It then follows that the number of hydrogen moles absorbed at the first collision is approximately equal to $km_{d,f}$. The rate constant k represents then a measure of the maximum number of hydrogen moles absorbed at the first collision.

The number $m_{d,1}$ of hydrogen moles absorbed when powders partially hydrogenated under static conditions undergo the first collision is approximately equal to 5.8×10^{-8} mol for the experiment carried out at the lowest intensity and to 2.1×10^{-7} mol for the other. The further absorption of such moles at the first collision can be intuitively related to the generation of new surfaces in the fraction of powder charge trapped between ball and reactor

walls. The arrest of the isothermal absorption process under static conditions is indeed believed to depend on the formation of a hydride layer of roughly uniform thickness at the surface of powder particles, which progressively hinders and then stops the diffusion of hydrogen atoms in the bulk [20, 22]. No absorption process can then take place despite the continuous interaction between gaseous hydrogen and Mg_2Ni surfaces when diffusion paths are saturated [20, 22]. Shear events occurring when a mechanical load is suddenly applied at collision can however fracture the hydride layers, thus generating reactive surfaces and opening additional diffusion paths. It is on such fresh surfaces that new hydrogen moles can be absorbed.

Further information on the microscopic details of the hydrogen uptake under dynamic conditions can be gained by comparing the number of moles absorbed at the first impact, $m_{d,1}$, with the total number $m_{s,s}$ of hydrogen moles absorbed per surface unit under static conditions. In particular, the ratio $r = m_{d,1}/m_{s,s}$ provides an estimate of the surface extension required to absorb $m_{d,1}$ moles of hydrogen under static conditions. It represents therefore a measure of the area of reactive surfaces generated at the first impact. For sake of clarity, attention will be hereafter focused on the experiments carried out at the highest intensity. Similar findings are obtained for the experimental data obtained at low intensity.

The ratio r indicates that the surface area required to accommodate 2.1×10^{-7} mol of hydrogen is approximately equal to 5.4×10^{-4} m². This is the reactive surface area generated by a collision event characterized by an energy of 0.168 J. Taking into account that the amount of powder involved in each impact is approximately equal to 5×10^{-4} g [1, 2, 4, 5, 12, 23], the corresponding specific area of reactive surface is roughly equal to 1.1 m² g⁻¹. The aforementioned values of surface area and specific surface area refer only to the first impact. The values of reactive surface area generated at successive impacts can easily be estimated by differentiating Eq. 1 with respect to the number n of collisions and multiplying the results by the proper combination of conversion factors. More specifically, the reactive surface area S generated at each impact can be expressed as

$$S = k \frac{m_{d,f}}{m_{s,s}} e^{-kn}. \quad (2)$$

The S values obtained from the experimental curves reported in Fig. 2 and describing the kinetics of hydrogen absorption under dynamic conditions are reported in Fig. 3. It can be seen that the area S of the reactive surface generated at each collision decreases as the number n of collisions increases. Such behavior can be connected with the depletion of reactant Mg_2Ni powders as hydrogenation

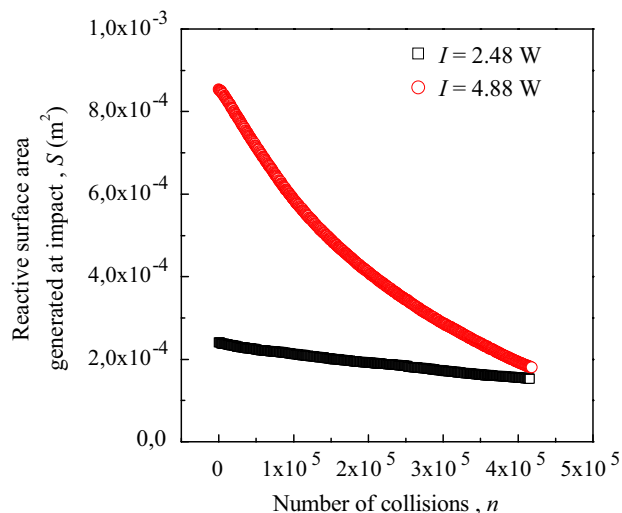


Fig. 3 The area S of reactive surfaces generated at each impact as a function of the number n of collisions. The intensity at which experimental trials were carried out are quoted

proceeds. The generation of non-hydrated reactive surfaces as a consequence of shear events at impact becomes indeed increasingly difficult due to the dissolution of hydrogen in the solid phase. With regard to this, it is worth noting that at the end of the dynamic absorption the total number m of moles absorbed by the 8 g of Mg_2Ni powders is expected to amount to about 0.102 mol. The latter value roughly represents the 70% of the total number of hydrogen moles, about 0.149 mol, necessary to completely convert Mg_2Ni into the hydride Mg_2NiH_4 phase. The decrease in the absorption rate can be then intuitively rationalized with the probability of exposing to the hydrogen atmosphere portions of unreacted surface. Of course, the probability of generating reactive surfaces decreases as the solid reactant decreases.

Along this line, it should be noted that the reactive surface area S of 5.4×10^{-4} m² produced when about 5.4×10^{-4} g of powders are processed at the first impact with an energy of 0.168 J does not represent the total surface area generated at the impact. Mg_2Ni powders are indeed subjected to dynamic absorption regimes once the hydrogen-absorbed moles amount to about 4.7×10^{-2} mol. This means that approximately the 30% of powders is hydrided. Therefore, roughly the 70% of the total surface area generated at the first impact can be involved in the hydrogen absorption process, whereas the reacted surface area represents the 30%. It follows that the total surface area generated in about 5.4×10^{-4} g of Mg_2Ni powders by a 0.168 J collision amounts approximately to 7.7×10^{-4} m². The latter estimate represents a rough measure of the total extension of the surfaces affected by shear events at collision when the average impact energy amounts to 0.168 J. The specification of the impact energy is of outstanding

importance being the total surface generated at impact strongly dependent on it. The value of total surface area drops indeed to $3.4 \times 10^{-4} \text{ m}^2$ for an average impact energy of about 0.084 J.

The knowledge of the initial rate of hydrogen absorption under static conditions, equal to about $2.6 \times 10^{-4} \text{ mol s}^{-1}$, allows for roughly estimating the time period τ necessary for a given reactive surface area generated at impact to absorb a known amount of hydrogen. Let us consider again the experimental data set collected at an average impact energy of 0.168 J. The number of hydrogen moles absorbed as a consequence of the first impact is about $2.1 \times 10^{-7} \text{ mol}$. The time period τ approximately corresponds to the ratio between the number of moles absorbed at the first impact and the initial static absorption rate and is equal to $8 \times 10^{-4} \text{ s}$. In the case of the experimental trial carried out at an impact energy of 0.084 J, τ amounts instead to about $2 \times 10^{-4} \text{ s}$. Although these numbers must be regarded only as rough estimates, they clearly point out that the time period τ during which absorption takes place is significantly lower than the time interval between successive impacts. Being the collision frequency N of about 29 Hz, successive collisions are separated by time interval $\sim 3.4 \times 10^{-2} \text{ s}$ long. The time period τ has instead a length comparable with the average duration of quasi-inelastic powder-trapping collision between ball and container walls, for which an upper boundary is evaluated on the order of $1 \times 10^{-3} \text{ s}$ [1, 2, 4, 5, 12, 23].

Conclusions

Under static conditions, 8 g of Mg_2Ni powders synthesized by mechanical alloying processes spontaneously absorb about 4.7×10^{-2} moles of hydrogen. Such number represents an estimate of the asymptotic value beyond which the static absorption process stops. Absorption re-starts under mechanical processing conditions with a kinetics of exponential character and is expected to determine on relatively long times the uptake of further 5.5×10^{-2} moles of hydrogen. This is a consequence of the entrapment of powder particles between ball and reactor walls at collision. Mechanical activation of powders can be here interpreted as an effect of reactive surfaces generated at each collision as a consequence of local shear events originating by the accommodation of forces within the volume of powders undergoing the sudden mechanical load. Once generated at impact, reactive surfaces are expected to undergo hydrogen absorption processes analogous to the ones occurring under static conditions. Reliable estimates of the area of reactive surfaces can be obtained as a consequence of an accurate characterization of the hydrogen absorption kinetics and of the knowledge of hydrogen absorption rates under static regimes. The time periods over which hydrogen

is absorbed on the reactive surfaces generated at each collision can be also roughly estimated, indicating that time scale of the absorption process is the same of the collision duration. This result is not surprising in the light of the extremely high frequency of impacts of the hydrogen molecules per surface unit, on the order of $1 \times 10^{27} \text{ mol m}^{-2} \text{ s}^{-1}$, at the pressure and temperature values defined by the experimental conditions. It is also worth noting that the surface area values and the characteristic absorption times strongly depend on the average energy at which collisions take place.

The detailed characterization of the kinetic behavior of the reacting system permitted then a reliable quantification of mechanochemical effects in terms of fundamental mechanochemical parameters such as area of surface involved in the absorption process at collision and characteristic absorption times. Systematic investigations on different chemical systems could then open the door to a deeper rationalization of the observed phenomenology and then to a further advance of fundamental knowledge.

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