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# Theoretical study of hydrogen desorption on $Mg_{50}Ni_{50}$ using statistical physics treatment

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ABSTRACT

In this work, $Mg_{50}Ni_{50}$ hydrogen storage alloy was synthesized by mechanical alloying technique, by using a planetary high energy ball mill (Retsch PM 200). The morphological and microstructural characterization of the powders was performed via scanning electron microscopy and X-ray diffraction. The dehydriding characterization of the composite was performed via a solid gas reaction method at different temperature 313 K, 333 K and 353 K. A new model has been developed, describing pressure-composition isotherms basing on statistical physics treatment. The monolayer model with two types of sites is found to fit very well with experimental data obtained on $Mg_{50}Ni_{50}$. The parameters involved in the model were determined directly from the experimental data by numerical simulation. The behaviors of these parameters are discussed in relationship with absorption and desorption process. Finally, the different thermodynamical potential functions are derived by statistical physics calculations from the adopted model.



## Introduction

Hydrogen storage in metal hydrides has attracted considerable interest of chemists, physicists and engineers for many decades. Metal hydrides have a higher storage capacity [1–4]. Moreover, they are safer than other hydrogen storage methods. Magnesium-based alloys are among the most promising materials for hydrogen storage. This thanks to their low specific weight, high storage capacity (H/M ratio), and low cost [5,6]. However, Mg-based alloys have a few limitation related to their poor hydriding/dehydriding kinetics and high absorption/desorption temperature. Researchers resorted to alloying magnesium with other elements [7] and to mechanical alloying [8] to overcome these shortcomings. Two intermetallic exist in the Mg–Ni system, that are, $Mg_2Ni$ and $MgNi_2$. During hydrogenation, $Mg_2Ni$ can store hydrogen up to 3.6 mass%. Moreover, it forms a hydride, $Mg_2NiH_4$, at higher hydrogen concentrations so as to yield a steady covalent-type bonding made up of $Mg^{2+}$ and $[NiH_4]^{4-}$ complex [9–12]. $Mg_2Ni$ has a faster hydriding and dehydriding kinetics than $MgH_2$, but lower storage capacity [13–15]. Differently from $Mg_2Ni$ no hydrogen absorption is seen/appears in intermetallic $MgNi_2$ [13]. In the equiatomic composition between the above mentioned two compounds, the amorphous Mg–Ni phase is formed by mechanical alloying [16–19]. Mechanical alloying (MA) developed by Benjamin et al. [20,21] in 1970s, is a

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technique for solid-state powder processing. This method can increase the specific surface area [22] and leads to microstructural refinement [23–25]. This brings about an improvement in hydriding/dehydriding kinetics [26–28]. Lianbang et al. [29] found that MA is very useful method for the synthesis of Mg-based hydrogen storage alloys, which have large surfaces area, low absorption temperature and high hydriding and dehydriding kinetics. It found that these alloys absorbed a large amount of hydrogen with a relatively high rate and its dehydriding commenced at around room temperature. They found also that the $H_2$ absorption temperature of MA $Mg_2Ni$ is 30 °C.

It has been reported that $Mg_{50}Ni_{50}$ amorphous alloys can be synthesized by mechanical alloying [30], and their hydrogen absorption properties have been investigated by several researchers [18,31–33]. Other researchers found that the maximum hydrogen absorption desorption capacity occurs during $Mg_{50}Ni_{50}$ amorphous phase in addition to the formation of an $MgNiH_{2.02}$ hydride [34,35].

For a hydrogen absorbing/desorbing alloy, P–C isotherms are among the key parameters in assessing the thermodynamic properties. These sorption isothermal curves allow following the evolution of hydriding/dehydriding reaction. Modeling is very important in understanding and analyzing metal hydride hydrogen storage systems. Various researchers [36–44] have described models for the P–C isotherms of hydrogen-absorbing alloys using statistical physics, thermodynamics and pure mathematical and empirical methods and have developed a few key parameters of the alloys.

In this paper, we present the methodology used to find new and simple theoretical expression that is able to describe and fit well the desorption isotherm of hydrogen on $Mg_{50}Ni_{50}$. The study is composed of two parts: in the first one, we use a statistical physics treatment to establish the expression of an adequate model giving the desorbed quantity against the pressure. In the second part, we apply the analytical expression to experimental data. Then we apply the model to interpret the desorption stereographic and energetic.

## Material and methods

The $Mg_{50}Ni_{50}$ alloy was synthesized by mechanically alloying (MA) of Mg (99.8%) and Ni (99.9%) in a 1:1 atomic proportion. Mechanical alloying (MA) was carried out using a planetary high energy ball mill (Retsch PM 200) in a stainless steel vessel at a speed of 300 rpm for 10 h. The phases and the microstructure were analyzed by X-ray diffraction (XRD) using a Philips Expert-PRO diffractometer with Cu $K_\alpha$ radiation. The morphology images were obtained by scanning electron microscopy (SEM) using a Philips XL20 microscope.

The hydriding/dehydriding characterization of the composite was performed via a solid gas reaction method at different temperature 313 K, 333 K and 353 K. The gas used is the hydrogen of the UP type 99.99%. The reactor and the reservoir are submerged in a bath in which the temperature is controlled by a thermostat with circulation (Julabo SC-3). The used reactor is cylindrical connected to the reservoir and composed of two parts made of brass: a cylindrical body and a lid. The pressure in reservoir is measured by a pressure gauge (type PA-21LC, 0–100 bar). The sensor of pressure is connected to a D.C. constant voltage and to a data acquisition system. The reactor tightness for vacuum (10 − 3 bar) and for hydrogen pressure of more than 16 bars was tested. It is important to note that a numerical study of the effect of different parameters using the model which was presented by Askri et al. has been carried out in order to choose the suitable dimensions of the reactor (diameter, height, thickness…) and the quantity of $Mg_{50}Ni_{50}$ alloy introduced in the reactor that permits to achieve quasi-isothermal conditions in the bed. Initially a primary vacuum is realized in the reactor and in the reservoir. Then a quantity of hydrogen is introduced in the reservoir under a determined pressure. When the reservoir is put in communication with the reactor, absorption of hydrogen by the alloy takes place and the pressure in the reservoir decreases until equilibrium. This operation is repeated at a constant temperature using a higher initial reservoir pressure until saturation of the hydride bed.

As for desorption, the reservoir, initially under a primary vacuum, was put in communication with the reactor. Then the pressure in the reservoir went up until reaching the equilibrium. This operation was repeated at a constant temperature, until obtaining a complete desorption.

The isotherm data are presented in Fig. 1.

## Microstructural and morphological characterization

Fig. 2 shows the powder diffraction patterns of 10 h milled $Mg_{50}Ni_{50}$ powders. As a general feature, the investigated alloy presented highly broadened diffraction peaks. These broad and low intensity peaks can be observed ranging from nearly 20 to 50°, indicating the predominance of an amorphous structure. Added to these two broad peaks, small broadened diffraction peaks are detected too. These characteristics suggest that the alloys possess microstructures constituted by two contributions: nanocrystalline and amorphous phase.

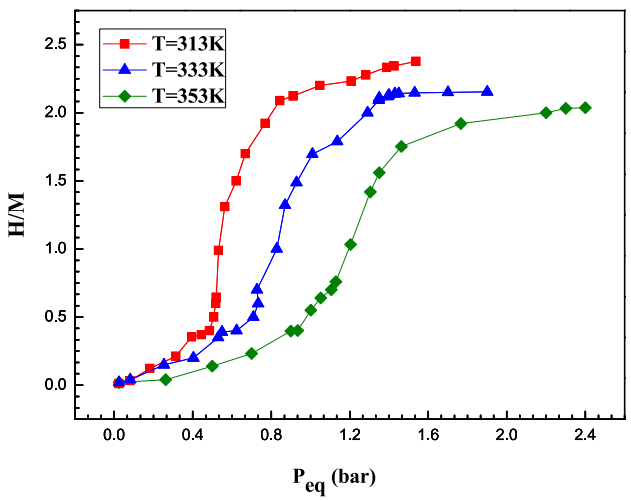


**Fig. 1 – P–C isotherms of $Mg_{50}Ni_{50}$ alloy at different temperatures.**

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