



Hydriding kinetics of Mg—TiH₂ fine dispersions obtained by mechanosynthesis

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ABSTRACT

Mg₈₀—Ti₂₀ hydride systems were prepared via reactive ball milling following two different procedures: grinding Mg with Ti or TiH₂, in both cases under H₂ atmosphere. Such systems were subjected to several cycles of hydrogen uptake and release in volumetric Sieverts apparatus under different pressure and temperature conditions. A structural characterization from SEM images and XRD patterns reveals no essential microstructural differences between the samples obtained by different routes, although a growth in domain size with temperature is observed. Also, the slowing of the kinetics when the temperature goes down is more pronounced in the specimen fabricated by the second route.

The influence of the transformed and untransformed phase fractions on the absorption kinetics can be well described using a double Hill function. Such complex function takes into account two distinguishable processes, with and without nucleation, that differentiate themselves as temperature increases. The first one may be related to surface absorption and the second tentatively ascribed to reactions at grain boundaries, dislocations and other extended defects.

The fitted values may then be associated to physical constants of the processes occurring during hydrogen absorption in both regions.

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1. Introduction

Solid hydrides are thought to be of crucial importance as hydrogen storage materials in global energy prospects based on hydrogen as an energy carrier. While Mg is nominally a good candidate for solid-state hydrogen storage, due to its capacity (up to 7.6 wt% H), availability and low cost, its sorption kinetics should be considerably improved for it to become of practical use in reliable applications. The reduction of grain sizes to the nanometer scale has demonstrated to be useful for reducing hydrogen uptake/release times [1,2]. Furthermore, the addition of small quantities of transition metals has been used with the objective of destabilizing the hydride. Kinetic properties can be significantly improved by combining a nanometric microstructure and the addition of metals. Particle size reduction shortens the length of the diffusion path for H atoms and produces a high surface density for H chemisorption. Additives such as transition metals facilitate H chemisorption and promote the dissociation of the H molecule. For example, sorption kinetics has been highly enhanced by milling Mg with several transition metals such as Nb [3,4,5], V [4,6], Pd [7] and Ni [8].

The Mg—Ti system is immiscible, so metastable alloys and hydrides can be produced either in thin film [9,10] by vapor deposition

or bulk geometries [11,12] via ball milling among others. These metastable phases constitute a promising route to destabilize magnesium hydride. Anastasopol et al. [13] reported a reduction in the formation enthalpy (−45 kJ/mol H₂) and entropy (−84 J/Kmol H₂) of hydrogenation of MgTi alloys made by spark discharge, but the thermal stability upon cycling is problematic, affecting their potential use for hydrogen storage. On the other hand, good cycling and kinetic results have been obtained in the MgH₂—TiH₂ system synthesized by reactive ball milling [14–17].

Ponthieu et al. [18] studied the Mg—Ti system, in particular Mg_{0.7}Ti_{0.3}, and concluded that it can store reversibly up to 3.7 wt% at 573 K without changes up to 100 cycles.

In previous work [19], we studied the formation kinetics and microstructure of Mg—Ti hydrides produced via reactive ball milling following two different routes. We found that alloying Mg with Ti or TiH₂ leads to very fine Mg—Ti dispersions with good hydrogenation properties without significant reduction in their hydrogen gravimetric capacity [20,21]. Indeed, the need for a hydrogen gravimetric density up to 6% [22] is well satisfied for Mg_xTi_(1-x) systems with x ≥ 0.7.

In the present work, we focus our attention on the study of the absorption kinetic properties in some of the samples fabricated via reactive ball milling. The 80:20 ratio was found to be satisfactory, accounting for the hydrogen wt% required with good formation kinetics [19].

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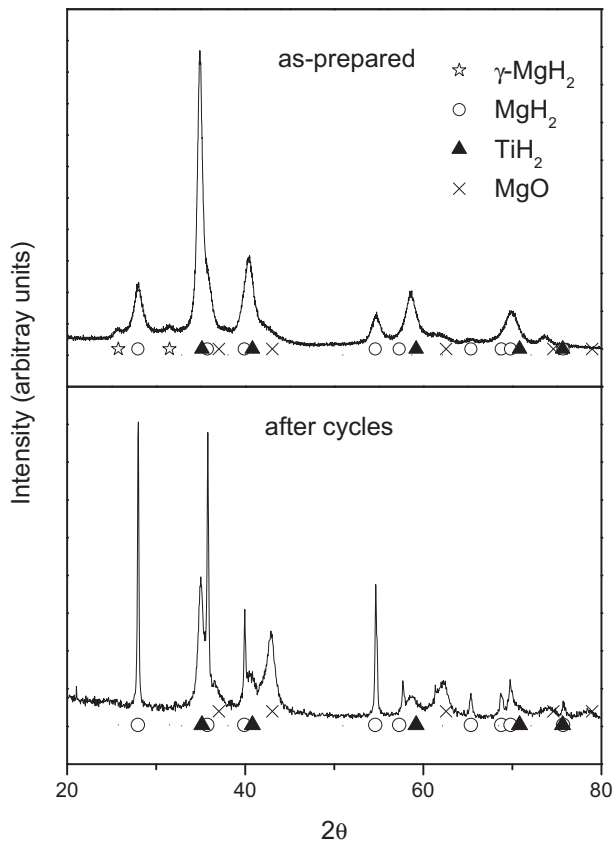


Fig. 1. Powder diffraction patterns for as prepared and after cycles specimens. Also are shown the peak positions for the main phases observed.

In studying the kinetics, different approaches have been employed to identify the processes involved, among them, the search for a *rate-limiting step* and the identification of *nucleation and growth processes* [23–27]. In the present work, a composite function with two additives

Hill functions [28]:

$$\chi(t) = \chi_1 \frac{t^{n_1}}{T_1^{n_1} + t^{n_1}} + \chi_2 \frac{t^{n_2}}{T_2^{n_2} + t^{n_2}} \quad (1)$$

is necessary to consistently fit the whole set of measured absorption curves. An interpretation in terms of two different regions, with distinct absorption behavior, is thus suggested.

2. Experimental

Mixtures of Mg—Ti in atomic ratio 80:20 were obtained from Mg granules and Ti powder of purity 99.9% and 99.4%, respectively. The mixtures were placed in a cylindrical steel milling vial together with one steel ball ($\phi = 12$ mm) and ground in an oscillatory ball mill in H_2 atmosphere (route *a*). A second group of samples was prepared from a mixture of Mg and TiH_2 (obtained also by mechanosynthesis), which was ground in H_2 atmosphere (route *b*). The details of the milling procedure and the resulting *formation* kinetics were described previously [19].

Sieverts type apparatus [29,30] was used to carry out several dehydrogenating and hydriding cycles on the studied systems as well as many thermal treatments. Specimens of 100–200 mg were extracted from the as-prepared powders and placed in the reactor, which consists of a stainless steel cylinder of about 0.6 cm³. A quartz wool filter was used at the extremes of the reactor, avoiding powder spreading outside the reactor. Temperature was measured with a PT 100 sensor in contact with the sample, inside the reactor. On the other hand, the instantaneous pressure P as a function of time was measured with a gauge transducer sensor. A configuration of manual and automatic valves was designed in order to perform different experiments controlling the initial pressure for absorptions and minimize the valve operation times. A standard known volume was used to determine the effective reactor volume at the working temperature.

Basically, two kinds of experiments were carried out. On the one hand, hydrogen desorption–absorption experiments at constant volume: first heating the sample from an uptake state at RT, and then cooling it again. Specifically, the temperature was increased up to

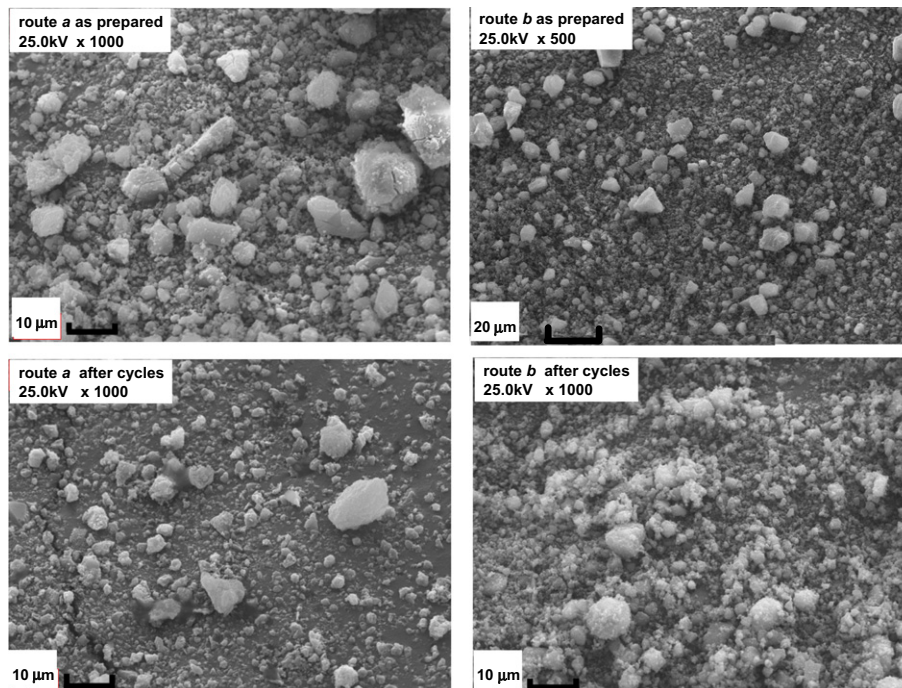


Fig. 2. SEM images for samples prepared through routes *a* and *b*, as prepared and after cycles.

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