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# Microchip power compensated calorimetry applied to metal hydride characterization

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ABSTRACT

In this work, we show the suitability of the thin film membrane-based calorimetric technique to measure kinetically limited phase transitions such as the dehydrogenation of metallic hydrides. Different compounds such as Mg, Mg/Al and $Mg_{80}Ti_{20}$ have been deposited over the active area of the microchip by electron beam evaporation. After several hydrogenation treatments at different temperatures to induce the hydride formation, calorimetric measurements on the dehydrogenation process of those thin films, either in vacuum or in air, are performed at a heating rate of 10 °C/min. We observe a significant reduction in the onset of dehydrogenation for $Mg_{80}Ti_{20}$ compared with pure Mg or Mg/Al layers, which confirms the beneficial effect of Ti on dehydrogenation. We also show the suitability of the membrane-based nanocalorimeters to be used in parallel with optical methods. Quantification of the energy released during hydrogen desorption remains elusive due to the semi-insulating to metallic transition of the film which affects the calorimetric trace.

## 1. Introduction

Hydrogen storage alloys are important materials for the future development of clean hydrogen energy systems and a number of promising metal hydrides have already been reported in the literature [1,2] and references therein. The advantage of metal hydrides comes from their ability to store hydrogen at low pressure but also from the fact that the hydrogen is released through an endothermic reaction, making hydrogen storage inherently safe. However, in spite of thousands of alloys screened up to date, no single composition meets all the requirements needed for its use in mobile applications [3]. Among the hydrides, Mg or Mg-based alloys are promising due to their relatively high percent storage weight capacity, though the high enthalpy of $MgH_2$ formation, around −78 kJ/mol $H_2$, remains a handicap for its commercial use [4,5]. In addition, high hydrogen pressures and high temperatures, 500 K, are typically needed to reach reasonable fast absorption rates in Mg bulk samples. Nevertheless, several authors have shown that the kinetics of hydrogen uptake/release can be greatly improved by reducing the grain size to the nanometer scale [6,7]. Also, to decrease the thermodynamic constraints and still promote the use of Mg-based alloys for hydrogen storage, various strategies have been experimentally tested and discussed [8,9]. Forming stable Mg-based compounds by adding elements that exhibit negative heats of mixing is a possible and suited route to lower the reaction enthalpy, as is the case of $Mg_2NiH_4$, however, at the expense of reducing the storage capacity of the base material. Another possible and better solution would

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come from adding light metals with a lower affinity to hydrogen, such as Al or other light group elements. The addition of Al to Mg has been already analyzed by several groups using combinatorial methods [10,11] assessing the presence of the alanate phase, $Mg(AlH_4)_2$, for certain compositions. Besides, recent studies have shown that $Mg_xTi_{1-x}$ alloys have excellent rate-storage capability and high reversible capacity without forming stable intermediate compounds [12]. These alloys also show fast switching between two optical states: absorbing in the hydride state and highly reflecting in the metallic state, which permits the applicability of these films as smart solar collectors [13].

Among the several techniques employed for the preparation of metal hydrides, the thin film deposition technique presents several advantages in the search for new compounds. The use of vapor phase methods enhances the control of the compounds purity, stoichiometry, structural order and grain size in comparison with bulk methods such as ball milling. In addition, diffusion limitations are also minimized in thin films and therefore the sorption/desorption of hydrogen is not kinetically limited. Furthermore, the minimal surface kinetic barrier in thin films can be eliminated, with the addition of a Pd cap layer that promotes desorption around 100 °C as already shown by Higuchi et al. [14]. This permits one to focus more easily on thermodynamic aspects which ultimately control the desorption temperatures. Unfortunately, the low amount of material, and consequently of hydrogen, complicates the use of conventional characterization methods such as thermogravimetry, differential scanning calorimetry or volumetry. To overcome this drawback, optical methods are more easily adapted and are actually being exploited to characterize the hydrogen absorption/desorption of metallic thin films [15,16]. Calorimetry is a versatile tool to analyze phase transformations as it allows the determination of kinetic and thermodynamic reaction parameters. An extension of the technique to measure phase transitions or reactions in thin film scale is therefore relevant to the scientific community. Up to now, membrane-based scanning nanocalorimetry has been scarcely used either in quasi-adiabatic or in non-adiabatic form at ultrafast heating rates for such purposes [17–19]. We have to note that in such scanning methods, the heating rate fundamentally depends on the current injected through the heater (power introduced into the calorimetric cell) and on the addenda (heat capacity of the calorimetric cell plus the sample loaded) and may also dramatically change during the phase transition depending on the sample mass and on the energy of the transition. To overcome this situation an active control of the heating process is required [20]. In addition, the determination of the onset temperature and the enthalpy involved in kinetically limited phenomena requires slower heating rates than those achieved in pulse-heating mode under quasi-adiabatic conditions. This is the case of hydrogenation/dehydrogenation reactions where the diffusion of hydrogen through the hydride is the limiting pathway; thus heating rates no higher than 10–20 °C/min are often required.

In previous works, we have shown the feasibility of membrane-based microdevices to be used in power compensation mode in a wide heating rate interval [20,21]. In this paper, we extend the methodology and demonstrate, for the first time to our knowledge, the use of membrane-based nanocalorimeters to analyze the dehydrogenation reaction in several metallic hydrides (pure Mg, Mg/Al and MgTi) thin films. We determine the influence of the alloy composition on the onset dehydrogenation temperature and show the suitability of the technique to be used in parallel with other optical methods. We also outline the difficulties encountered to quantitatively determine the enthalpy of the transition. Taking advantage of the use of vapor phase deposition techniques for the material preparation and a membrane-based nanocalorimeter chip for the characterization, this work can be considered as the first step for the development of a combinatorial deposition methodology coupled with a high throughput characterization technique based on the discrete deposition of selected composition on microchip arrays to discover new materials for hydrogen storage.

## 2. Experimental

### 2.1. *Nanocalorimeter microchips*

The membrane-based calorimeters described in this work rely on a free-standing silicon nitride (500-nm-thick) membrane with areas of 4 × 4 and/or $5 \times 5\,mm^2$ supported by a silicon frame. A metallic thin film is patterned on top of the membrane to define the heater/sensor element (see schematic view of Fig. 1). Further details on the microdevice characteristics have been reported elsewhere [22,23]. Compared with previous designs the sensing area has been significantly increased to enhance the signal-to-noise ratio during the transformation. Introducing a pulse of current ($I$) the metal is heated by Joule effect. In a typical calorimetric experiment the Pt resistor served both as a heater and as a thermometer. The average temperature of the membrane is monitored by the variation in resistance with temperature. Because of the reduced thickness of the different elements forming the calorimetric cell, the temperature of the membrane and the metallic heater can be assumed to be equal, whatever the heating rates. The tensile state of the 480-nm silicon nitride membrane and the specific shape of the metallic heater have been previously optimized to preserve mechanical stability at medium to high temperatures and to minimize temperature differences inside the sensing area [23]. Although the mechanical stability of the membranes is outstanding excess manipulation and improper handling may result in membrane rupture. With alumina-capped Pt heaters, the calorimeter works nicely at moderate temperatures, 700 K, without exhibiting degradation of the electrical properties [23] even with the presence of hydrogen. The geometry of the chip allows for the sample deposition by vapor phase techniques using suitable shadow masks or by manual location on the backside of the chip membrane.

### 2.2. *Thermal modeling*

At moderate heating rates, 10–20 °C/min, and due to the reduced thickness of the membrane, the sample and the