

Coupled manometric – calorimetric measurements on Mg-based materials for H₂ storage

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Introduction: in recent years, increased efforts are under way to develop materials with reversible H₂ storage properties meeting the targets for on-board applications fixed by the US Department of Energy. At this respect, it is fundamental to evaluate with accuracy both the thermodynamic and the kinetics sorption properties of the candidate materials.

On the analytical point of view, the coupling between a manometric technique (PCTPro) and a calorimetric technique (Sensys DSC) is very interesting as both the absorbed/desorbed volume of hydrogen together with the corresponding enthalpy is measured on the same sample.

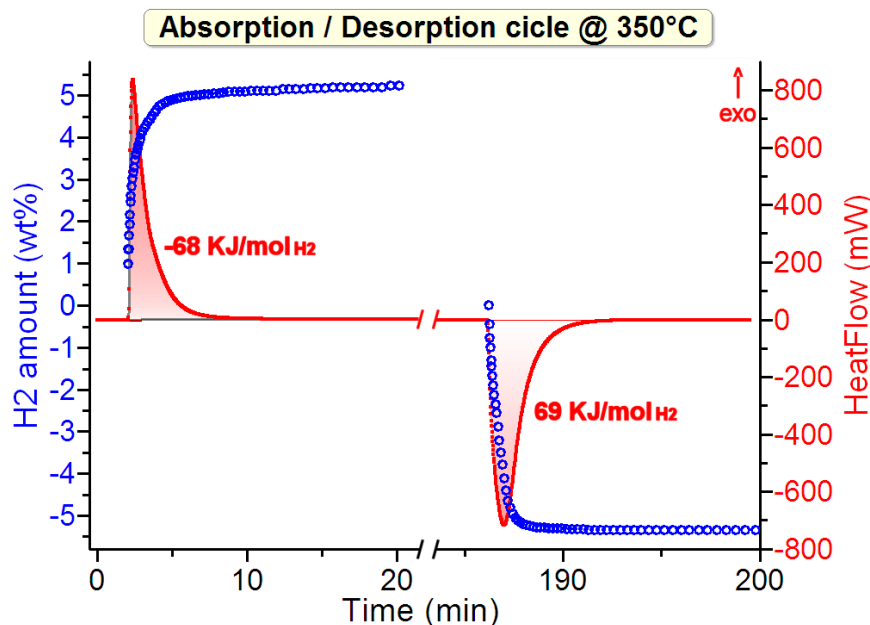


Figure 1

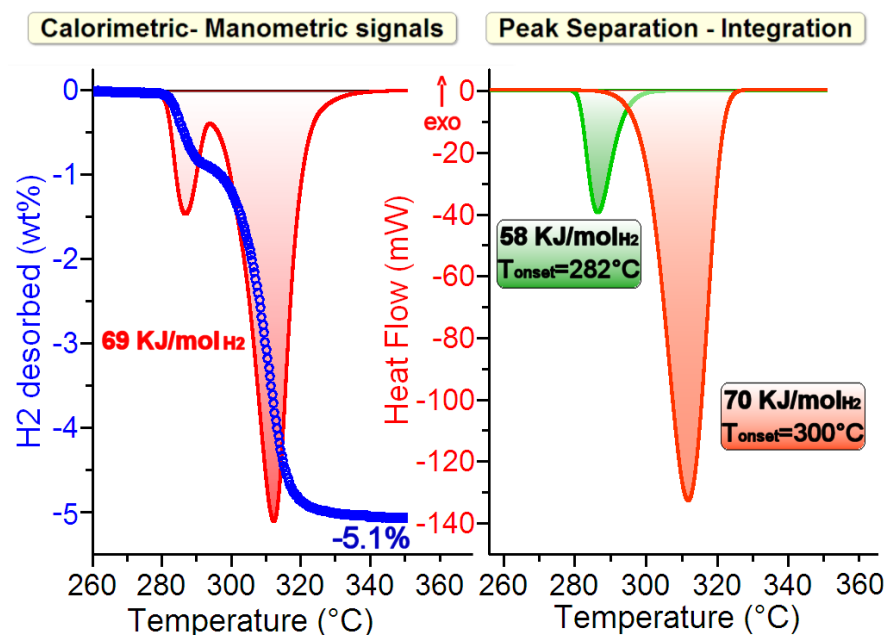


Figure 2

Experimental

About 30 mg of Mg 80.75 wt% – Ni 14.25 wt % – C 5 wt% composite prepared by mechanical milling were charged in the high-pressure cell of the Sensys DSC under Ar in the glove box. The cell was introduced in the Sensys furnace and directly connected to the PCT-Pro 2000 using a 1/8" Swagelok tube.

The sample was activated by 10 charging/discharging runs at 350 °C and H₂ pressure equal to 15 bar/0.9 bar (Figure 1).

Subsequently it was re-charged at 15 bar and 350 °C and cooled down at 200 °C at 10 °C/min before a TPD measurement was performed by heating at 2 °C/min up to 350 °C under H₂ pressure equal to 0.9 bar (Figure 2).

The volumetric and calorimetric data that are shown on figures 1 and 2 are obtained simultaneously on the same sample.

Data acquisition and treatment are obtained via the Calisto software.

Results

At the end of the activation procedure (Figure 1), the sample reversibly exchanges 5.4 wt % H₂, i.e. a value higher than the DOE target for 2010 (4.5 wt %). Up to 5 wt % H₂ is absorbed/released in 2 min/4min respectively. The hydrogenation/dehydrogenation enthalpy values (-68 kJ/mol H₂ and + 69 kJ/mol H₂ respectively) are very close and lower than the value obtained for pure MgH₂ (74.5 kJ/mol H₂).

Two desorption steps can be distinguished in the TPD profile (Figure 2), the low temperature one (282 °C) due to the dehydrogenation of Mg₂NiH₄, the high temperature one (300 °C) attributable to MgH₂ dissociation. The desorption enthalpy values obtained by the deconvolution of the peaks (58 kJ/mol H₂ and 70 kJ/mol H₂) are once again well lower than the data reported in literature for the pure compounds dehydrogenation (64.5 kJ/mol H₂ and 74.5 kJ/mol H₂ respectively). The integration of the whole signal gives a value equal to that obtained in isothermal conditions (Figure 1). All these data underlines the good destabilizing effect played by C towards the Mg/MgH₂ and the Mg₂Ni/Mg₂NiH₄ systems.

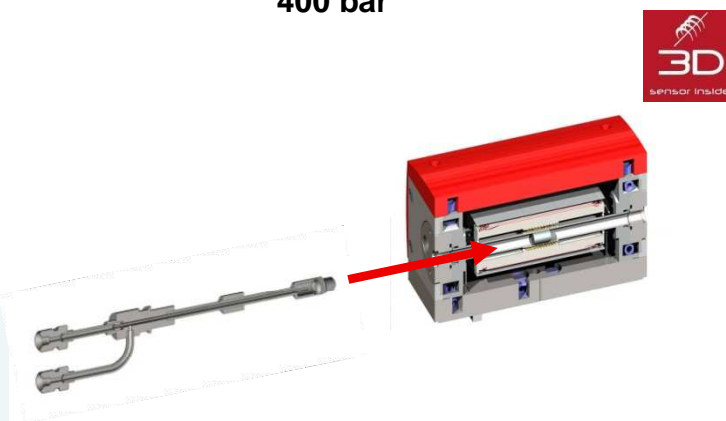
Instrument

PCTPro-2000
Gas sorption
Sievert's
instrument
-260 to 500°C



Instrument

Sensys HP DSC
Calvet 3D DSC
Up to 600°C
400 bar



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