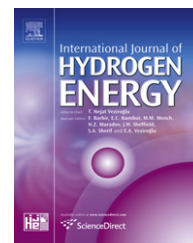


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Surface modification of TiFe hydrogen storage alloy by metal-organic chemical vapour deposition of palladium

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ABSTRACT

TiFe-based hydrogen storage materials are highly sensitive towards gas impurities which induce a significant deterioration of the hydrogen absorption performances. An efficient solution to this problem is in modification of the material surface by the deposition of metals (including Palladium) capable of catalyzing the dissociative chemisorption of hydrogen molecules. In this work the surface modification of TiFe alloy was performed using a metal-organic chemical vapour deposition technique (MOCVD), by the thermal decomposition of palladium (II) acetylacetonate ($\text{Pd}[\text{acac}]_2$) mixed with the powder of the parent alloy. Such a treatment was shown to result in the formation of coatings comprised of palladium nanoparticles, which subsequently facilitate the hydrogenation of the material even after its exposure to air, which otherwise prove detrimental. However, the hydrogenation performances were found to be quite sensitive to MOCVD conditions that, most probably, originates from side processes in the interaction of gaseous products of $\text{Pd}[\text{acac}]_2$ decomposition with TiFe.

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1. Introduction

Solid state hydrogen storage in metal hydrides (MH) is a promising technology in certain niche applications where system weight is not crucial, but where compactness, safety and technological flexibility are critical issues. An important factor in the implementation of MH hydrogen storage technology is the utilization of suitable hydrogen storage materials characterised by fast and reversible hydrogen uptake and release under mild conditions, in combination with low cost and availability, including feasibility of their manufacture based on local resources.

TiFe intermetallic compound is one of the most promising hydrogen storage alloys, due to its reasonable reversible hydrogen storage capacity (~ 1.8 wt% H) at near-ambient conditions, abundance and low cost [1,2]. The main drawback of TiFe and its derivatives is that they have poor activation performances and poisoning tolerance resulting in significant deterioration of hydrogen sorption even by trace amounts of gas species, including oxygen and water vapour [3,4]. An efficient solution to this problem is in the modification of the surface by encapsulation with a metal overlayer which catalyzes the dissociative chemisorption of hydrogen molecules [5]. Various methods of surface modification of

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a range of metallic hydrogen storage materials, including deposition of metal coatings, were shown to significantly improve performances of MH in both electrochemical and gas phase applications [6–14]. The improvements are more pronounced for surface modification by the deposition of palladium, which has superior catalytic activity towards dissociative H_2 chemisorption.

Reports regarding the introduction of Pd additives onto TiFe substrate by ball milling [15], physical vapour deposition (PVD) [16], or wet chemical autocatalytic deposition [17] are available. In all cases the improvement of activation performances and hydrogenation kinetics of the surface modified materials was observed. The listed methods, however, have a number of drawbacks including long process time and high power consumption (ball milling), complex hardware and low

productivity (PVD), high consumption and incomplete utilisation of expensive Pd precursor (wet chemical autocatalytic deposition).

The chemical vapour deposition of metal organic substances (MOCVD) was identified as a suitable alternative for the deposition of catalytic layers on the surface of MH. This technique is attractive due to its simplicity, flexibility, ability to be scaled up to industrial-scale production with relative ease, and the wide range of precursors available. The technique involves the transport of volatile precursor molecules (group-III metal-organics and group-V hydrides or alkyls) by a carrier gas (Ar , N_2) onto a heated substrate, where surface chemical reactions will occur to form thin layers of the metal. The MOCVD technique is also known to facilitate the deposition of small amounts of finely dispersed catalytic particles on the surface of

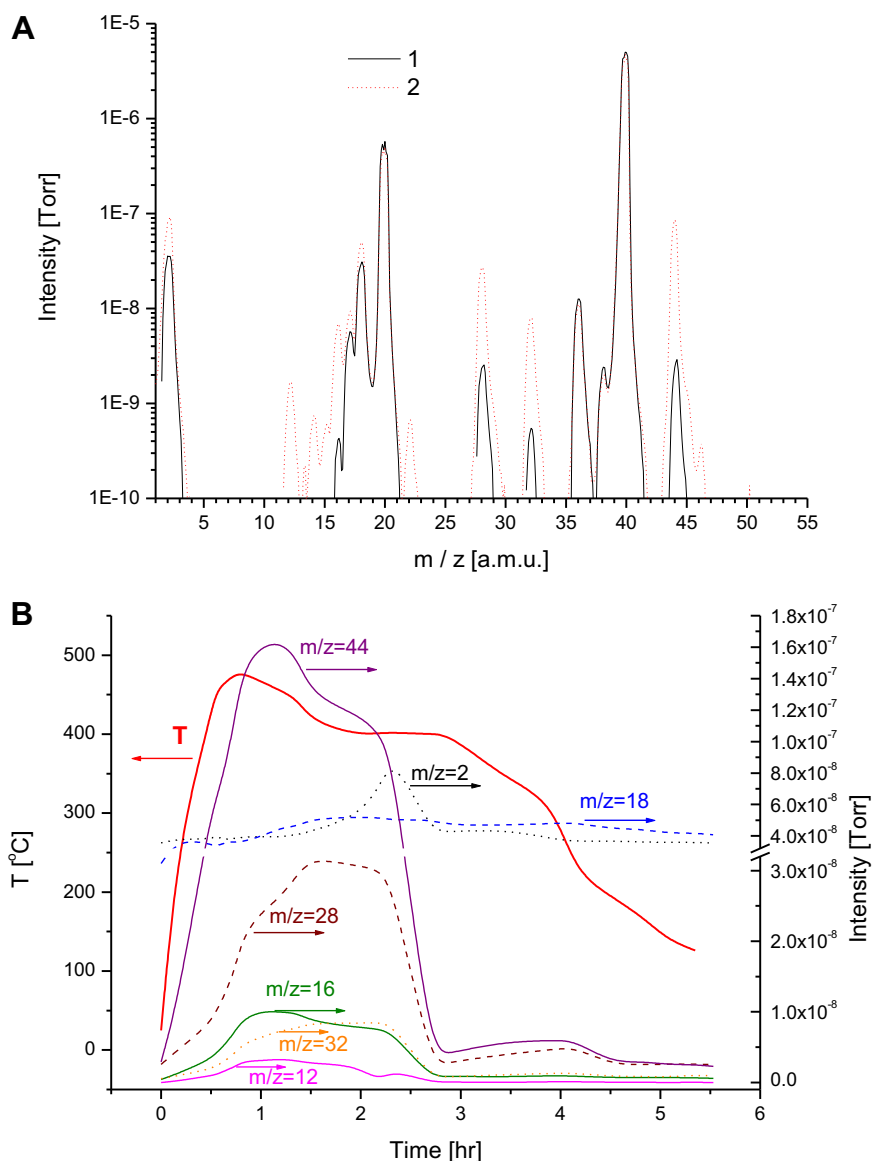


Fig. 1 – Mass spectrometric analysis of gas from running-flow reactor during MOCVD of Pd (5 wt.%) onto TiFe by thermal decomposition of $Pd[acac]_2$. Flow rate of the carrier gas 0.5 L/min. **A** – mass spectra of the gas before heating (1) and after 2.3 h of heating (2; $T = 402\text{ }^\circ\text{C}$); **B** – change of reactor temperature (T) and intensities of main impurity peaks during the MOCVD process.

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