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Catalysis and evolution on cycling of nano-structured magnesium multilayer thin films

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ABSTRACT

This paper explores the hydrogen cycling properties of Mg/Cr and Mg/V multilayer thin films and studies the effect of chromium and vanadium transition metal catalysts on the cycling properties of thick magnesium coatings. Two transition-metal catalysed magnesium-based multilayer PVD coatings are compared with a non-catalysed magnesium control sample. The (micro-)structural evolution of the thin film coatings into fine, flakey powders is studied in-depth using XRD, SEM and TEM and the hydrogen storage properties of all three materials are assessed using volumetric, gravimetric and calorimetric methods focussing on the effect of the microstructure and composition of the coatings on the hydrogen storage kinetics. It was found that the chromium-catalysed coating had the most favourable hydrogen storage kinetics with an activation energy for the dehydrogenation reaction of $65.7 \pm 2.5 \text{ kJ mol}^{-1}$ and a hydrogen capacity of $6.1 \pm 0.3 \text{ wt} \%$. The mechanism of the dehydrogenation reaction of the catalysed samples was studied using the CV and JMAK kinetic models and it was found that the catalyst material influenced not only the hydrogen storage kinetics but also the mechanism of the reaction.

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1. Introduction

Hydrogen is a versatile energy carrier that has applications ranging from consumer electronics to heavy-duty machinery. Its aggregate state and density at ambient conditions however make efficiently storing large quantities of hydrogen in a small volume challenging. Unlike compression and liquefaction of hydrogen, solid-state hydrogen storage can offer a cost- and energy efficient way of storing large amounts of hydrogen. Magnesium hydride is both relatively cheap and abundant and together with its high gravimetric and volumetric hydrogen storage capacity of 7.7 wt% and $0.11 \text{ kg H}_2 \text{ l}^{-1}$

respectively that makes it a favoured material for practical applications. Overcoming the challenging thermodynamic and kinetic limitations of the material, requiring temperatures above $300 \text{ }^\circ\text{C}$ in practice, has been the focus of a wide range of research activity. Many attempts have been made to reduce the temperatures required to reversibly store hydrogen in magnesium-based materials including the addition of transition metals and their oxides to form catalysed structures resulting in faster kinetics at lower temperatures including a range of systems using thin film techniques to incorporate these catalysts into the magnesium-based material. Examples include systems of Mg–Pd [1,2] Mg–Ti [3,4] and

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Mg–Ni [5,6]. Previous work [7] has shown improved kinetics for a magnesium-based multilayer system catalysed by a nickel-rich transition metal mix. Alloying of magnesium and nickel leads to a two-phase hydrogen storage system of MgH_2 and Mg_2NiH_4 catalysed by transition metal elements such as chromium and iron. This work investigates the effect of chromium and vanadium on the kinetics of magnesium multilayer thin films.

2. Experimental methods

A Teer Coatings UDP 650 closed field unbalanced magnetron-assisted physical vapour deposition (PVD) system, based on an argon plasma, was used to produce a range of different thin film multilayer coatings, consisting of layers of magnesium (purity 99.9%), separated by layers of chromium (Mg/Cr) and vanadium (Mg/V) transition metal catalysts (target purity 99.95%), and capped on both surfaces with a thin (14 nm) layer of palladium (target purity 99.99%) to prevent oxidation of the thin film and interaction with the substrate. In order to try and prevent any MgPd alloy formation as described by Tan et al. [4], a transition metal layer was deposited on the inside of both Pd capping layers. In addition, a magnesium control sample ($\text{Mg}_{\text{control}}$) was produced by depositing 150 layers of magnesium, under the same processing conditions used for the Mg/Cr and Mg/V samples, without transition metal interlayers, capped with 14 nm of Pd on both sides.

The PVD system enabled large surface areas to be coated generating ca. 300 mg of coatings that were delaminated from the glass substrates in acetone post deposition. 150–190 mg of each of the samples was then cycled up 60 times in a Setaram PCTpro sievert apparatus at selected temperatures between 250 °C and 350 °C under hydrogen pressures up to 2 MPa in order to study the kinetic behaviour and structural changes of the material.

The microstructure of the thin films was assessed both before and after hydrogen cycling by X-ray diffraction (XRD) on a Bruker D8 Advance diffractometer emitting monochromated $\text{CuK}\alpha$ radiation with a wavelength λ of 1.5418 Å through a 0.6 mm slit at 40 kV and 40 mA, in a Bragg-Brentano $\theta - 2\theta$ configuration. A series of locked-coupled $\theta - 2\theta$ scans were performed with a step size fixed at 0.05° a dwell time of 5 s per step for the as-deposited thin films and step size of 0.03° a dwell time of 10 s per step for the samples post cycling. For peak broadening analysis instrumental broadening was determined using a LaB_6 reference sample.

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) analysis was done on a high resolution Philips XL30 ESEM-FEG with an Oxford Instruments silicon drift EDX detector to determine the composition and overall layer thickness of the coatings' cross-sections, as well as the morphology of the thin films post-cycling. Transmission electron microscopy (TEM) and EDX analysis was performed on a JEOL 2100F (post cycling) microscope fitted with an Oxford Instruments INCA EDX system. The TEM sample preparation was done by suspending a small amount of the powder in acetone and pipetting a drop of the suspension onto a holey carbon grid. The same microscope was used to produce cross-sectional TEM images of the as-deposited Mg/Cr sample following sample preparation on a FEI

Quanta200 FIB/SEM. A Philips Tecnai F20 microscope was used to analyse the cross-section of the as-deposited Mg/V sample, a lift-out of which was prepared using a FEI Quanta3D FIB/SEM.

The dehydrogenation reaction of the sample was studied using differential scanning calorimetry (DSC) (Netzsch 204HP) using heating rates of 2 °C min^{-1} , 5 °C min^{-1} and 10 °C min^{-1} under 0.1 MPa of flowing Ar at a rate of 100 ml min^{-1} . A Netzsch 209 F1 Iris thermobalance was used for thermogravimetric analysis (TGA) of the samples under a flow of 100 ml min^{-1} of argon at atmospheric pressure, using a heating rate of 10 °C min^{-1} from room temperature to up to 500 °C.

3. Results

3.1. Structural analysis

The results of the X-ray diffraction study undertaken on the as-deposited thin film coatings are presented in Fig. 1. It is evident from the diffraction patterns that there is strong directional growth of HCP Mg-crystals in the $\langle 001 \rangle$ direction in all samples, indicated by diffraction peaks only in the (002) and (004) planes at 34.4 and 72.5° 2θ and there are peaks coming from the (111) planes from the palladium capping layers at 40.1° 2θ . In none of the samples is there any evidence of crystalline catalyst phases.

Similarly, Fig. 2 shows diffraction patterns taken for the three thin film samples in their hydrogenated state after 60 cycles of hydrogenation and dehydrogenation. It is clearly visible that the samples have all undergone similar changes in their microstructure, evident by the emergence of β -magnesium hydride and Mg_6Pd phases in all three samples. In the two catalysed samples there is also evidence of crystalline phases of BCC chromium (Mg/Cr) and BCC vanadium (Mg/V)

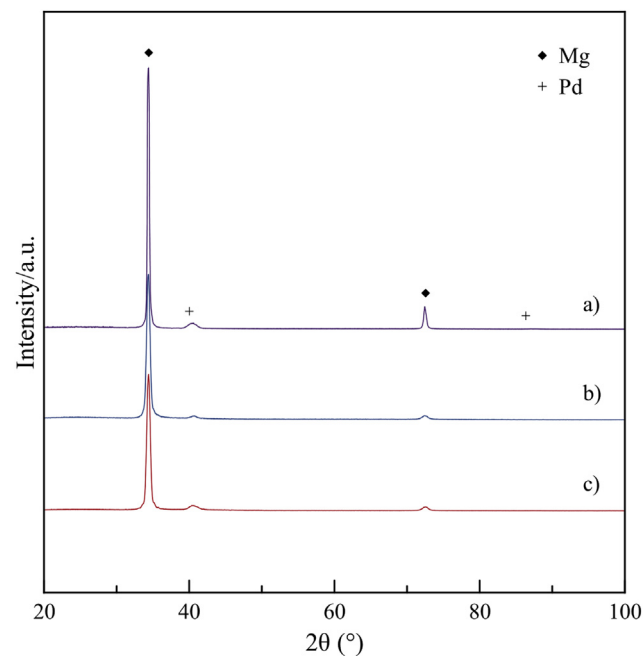


Fig. 1 – XRD pattern of the a) $\text{Mg}_{\text{control}}$, b) Mg/V and c) Mg/Cr thin films in their as-deposited state.

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