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COMMUNICATION

Effect of alloying magnesium with chromium and vanadium on hydrogenation kinetics studied with neutron reflectometry†

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The effect of chromium and vanadium alloying on the hydrogenation of a magnesium thin film is studied by neutron reflectometry. Immediate formation of a blocking MgD_2 layer is observed in pure Mg, however in the alloyed film deuteration is rapid and almost completely homogeneous.

Magnesium hydride has very high reversible storage capacity of 7.6 wt.% but suffers from extremely slow sorption kinetics and high stability ($-77 \text{ kJ mol}^{-1} \text{ H}_2$). The kinetic limitations are mostly due to extremely poor hydrogen diffusivity ($\sim 10^{-20} \text{ m}^2 \text{ s}^{-1}$ at 200°C)¹ through the hydride. Formation of a continuous layer of MgH_2 has often been observed to effectively block further hydrogenation when the particles are too large.^{2–4}

Although the stability is a very important issue, the vast majority of efforts are directed at improving the kinetics. One possibility is to try and eliminate the diffusion limitations by reducing the grain size and/or particle size, typically to 10 nm or less.^{5–7} Another possibility is preparation of composite materials. If the additives preferably alloy with each other and not with Mg, they form a separate catalyst phase which acts as a diffusion pathway through hydrided material. Al–Ti^{8,9} and Fe–Ti⁹ have already been proved to work very well.

The combination of Cr and V is expected to work in a similar manner as Fe–Ti as neither forms alloys with Mg, V has appreciable hydrogen solubility and diffusion is usually very rapid in bcc metals.¹⁰

Fig. 1 shows the absorption kinetics of the 1st, 5th, 10th and 20th cycle for a free-standing $1.5 \mu\text{m}$ thick cosputtered Mg–10%Cr–10%V film (ESI†). For this catalytic mixture, extremely fast absorption kinetics are observed. After 10 cycles, 90% of the total capacity is absorbed within 10 seconds, which is similar to what was observed for other Mg–TM cosputtered films.⁹

Hydrogen sorption measurements cannot distinguish the individual contributions of surface dissociation, diffusion and phase transformation to the ‘overall’ kinetics. Therefore, an

Fig. 1 Absorption kinetics of a $1.5 \mu\text{m}$ Mg–10%Cr–10%V film for the 1st, 5th, 10th and 20th cycle at 200°C . Absorption pressure was 2.5 bar.

in situ technique with high spatial resolution is required to separate bulk (diffusion, nucleation) and surface (dissociation) effects in real-time. To that end, we used Neutron Reflectometry (NR) which allowed us to determine the hydrogen/deuterium concentration as a function of depth with nanometre resolution.

We applied NR to study the deuterium absorption at room temperature of $5 \text{ nm Pd}/5 \text{ nm CrV}/50 \text{ nm Mg}(-10\%\text{Cr}-10\%\text{V})/10 \text{ nm Ta/Si}$, deposited on Si(100) substrates. Although interfacial effects between Mg and Pd may improve the desorption kinetics,¹¹ using a bilayer catalyst has been found by several authors to improve the absorption kinetics compared to having Pd in direct contact with a Mg(alloy) layer.^{12–15} Hence, our choice is for Pd/CrV in this study. Since deuterium can only enter the sample through the exposed bilayer catalyst, determination of the deuterium concentration depth-profile over time should elucidate the effects of alloying the Mg on the rate of deuterium penetration through the stack.

Fig. 2 shows the measured neutron reflectivity curves during absorption of the pure Mg (top panel) and Mg–10%Cr–10%V layers (bottom panel). A sensitive indicator of deuterium absorption is the critical scattering vector $q_c = 4(\pi Nb)^{1/2}$ below which there is total reflection,¹² where N is the total number density of scatterers in the layer and b is the average scattering length. The product Nb is called the Scattering Length Density (SLD). Due to the large scattering length of deuterium ($b_D = 6.67 \text{ fm}$),¹⁶ the increase in q_c is the first

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† Electronic supplementary information (ESI) available: Experimental conditions, model parameters corresponding to all SLD profiles in Fig. 3, reflectivity curves that were not shown in Fig. 2 and AFM micrographs. See DOI: 10.1039/c0cc05501h

Fig. 2 Measured reflectivity curves (open symbols) and fits (solid lines) for a 50 nm pure Mg (top) and Mg-10%Cr-10%V (bottom) film in as-deposited and partially absorbed states at room temperature. P_{D_2} for Mg was 50 mbar (ESI†), for Mg-10%Cr-10%V 10 mbar.

indication that the layers are absorbing deuterium. This is clearly observed in Fig. 2 where q_c increases monotonically with time, both for the Mg and Mg-10%Cr-10%V layers.

From the measured reflectivity data, SLD profiles were generated using Parratt's recursive algorithm, which yields the SLD as a function of depth as shown in Fig. 3. Interfacial roughness is accounted for in this approach.¹⁷ The solid lines in Fig. 2 are the reflectivity curves corresponding to these SLD profiles. As can be seen from Fig. 2, the simulated and experimental reflectivity curves agree quite well.

The SLD profiles as a function of time for the pure Mg layer are shown in the top panel of Fig. 3. In the top part of the Mg layer the SLD sharply increases immediately after absorption starts. After this, the rate of deuteriation decreases significantly and even after 20 hours the layer is not completely absorbed. A clear gradient in the deuterium concentration, which is modeled as two separate layers with high interfacial roughness, is clearly present in the middle of the layer. This strongly indicates the formation of a blocking layer of MgD_2 .

The deuterium content in a layer can be calculated as:¹²

$$C_D = \left[\frac{S_{M+D}}{S_{p=0}} \frac{t_{M+D}}{t_M} - 1 \right] \frac{b_M}{b_D} \quad (1)$$

where C_D is the deuterium concentration in D/Metal, S_{M+D} and $S_{p=0}$ are the SLD in loaded and as-deposited states, respectively, and t_{M+D} and t_M are the corresponding thicknesses. b_M and b_D are the scattering lengths of the metal and deuterium, respectively. The D/M ratio in the Mg layer is estimated as 0.44, 1 and 1.2 after 1, 10 and 20 h, respectively. After 1 h, the D/M ratio in the Ta layer is only 0.2 and slowly increases to 0.5 after 20 h.

Fig. 3 SLD depth profiles for a pure Mg film in as-deposited state and as a function of time at 50 mbar absorption pressure (top panel) at room temperature. Same for Mg-10%Cr-10%V in the as-deposited state, after 10, 20, 30 min and 6.5 h at 10 mbar and finally 1 bar (bottom panel).

The interfacial roughness between the layers increases rapidly to a point at which the Pd and CrV layers are no longer distinguishable from one another. Therefore, a single layer with an SLD between that of Pd ($4.02 \times 10^{-6} \text{ Å}^{-2}$) and CrV ($1.4 \times 10^{-6} \text{ Å}^{-2}$) was used to fit the reflectivity curves, as can be seen from Fig. 3. The root-mean-square roughness (R_q) found from the fit for the 'catalyst'/D₂ and Mg/'catalyst' interfaces are 25 Å after 1 h and 32 and 34 Å, respectively, after 20 h.

Atomic force microscopy (AFM) was performed on the Mg layer, both in as-deposited and hydrogenated states to get a measured value for R_q of the catalyst/D₂ interface. The R_q values found for the as-deposited state are 9.1 and 9.2 Å from fitting the reflectivity curve and AFM measurement, respectively. After hydrogenation, the roughness measured with AFM had increased to 21.4 Å (ESI†). This is lower than the 32 Å found from the fit to the neutron data, but because of tip dilation effects in AFM, the value found with this technique will always be lower than the actual value.

Significant differences between the behavior of Mg-10%Cr-10%V and the pure Mg layer are immediately obvious from Fig. 3 (bottom panel). The Ta layer on the bottom of the stack attains its final SLD immediately after the first measurement at 10 minutes. Another remarkable feature in the SLD profiles is that the thickness of the Mg alloy layer is identical to the as-deposited state, despite the fact that the deuterium concentration increases to 0.25 and 0.5 D/M after 10 and 20 minutes, at 10 mbar pressure. The top part of the Mg-Cr-V layer has already reached its final SLD after only 30 minutes. There is a small gradient in the deuterium concentration, but there is no evidence of a blocking layer.

Fig. 4 XRD patterns of (a) as-deposited 50 nm Mg–10%Cr–10%V, (b) as-deposited 500 nm Mg–10%Cr–10%V tilted to $\chi = 60^\circ$, (c) hydrogenated 50 nm Mg and (d) hydrogenated 50 nm Mg–10%Cr–10%V.

Between 20 and 30 minutes, the thickness of the Mg alloy layer increases from 554 Å to 710 Å and finally 718 Å when the layer is fully saturated, which is an expansion of 29.6%. The final D/M ratio in the Mg alloy layer calculated with eqn (1) is 1.54, which is close to the expected maximum value of 1.6 (= 2 D/Mg). For the Pd and CrV layers, these values are 0.07 and 0.26, respectively, at 1 bar pressure. Thus, based on our measurements, a maximum 0.052 of the 1.54 D/M can be contributed by Cr and V.

Both films were investigated by X-ray diffraction in their as-deposited and hydrogenated states. As shown in Fig. 4, the layer is strongly (002) textured. The (101) peak was also detected by tilting the sample, enabling calculation of both lattice parameters as $a = 3.17$ and $c = 5.12$ Å. The unit cell volume is ~6% larger than expected based on a linear combination of the molar volumes of Mg, V and Cr. The Mg grain size is determined as 246 Å from the integral breadth of the (002) peak using the Scherrer equation (ESI†).

XRD measurements confirmed the formation of crystalline MgH₂ for the Mg layer which explains the blocking effect that was observed in Fig. 3. For Mg–10%Cr–10%V, the position of the MgH₂ (110) reflection is identical, which means all Cr and V segregate from Mg upon hydrogenation. The crystallite sizes of MgH₂ are 119 Å for pure Mg vs. 56 Å for the alloy layer. The smaller grain size also makes the alloy film much smoother; R_q determined with AFM was only 6.1 Å (ESI†).

The Cr–V phase appears to limit the MgH₂ grain size by forming a networked structure along the grain boundaries. Such a network would serve as a rapid diffusion pathway for deuterium as well as providing a high number of heterogeneous nucleation sites for MgH₂. This explains the absence of a blocking layer in Mg–10%Cr–10%V and the almost homogeneous increase in SLD observed in Fig. 3. For the Mg layer, the only heterogeneous nucleation site is at the interface between the CrV and Mg layers leading to a blocking deuteride layer. Nucleation also appears more difficult there as the required pressure was 5× higher compared to Mg–10%Cr–10%V (ESI†).

Based on the XRD results, up to 6% volume expansion due to deuteration can be compensated for by segregation of the Cr and V. Absorption of 0.5 D/M is expected to expand the film by ~3% compared to the as-deposited state (9% compared to the

segregated state). This suggests that some ‘excess’ deuterium can be stored in the first cycle, which may account for the slightly higher capacity observed in Fig. 1. The expected total expansion is 21%, which is significantly lower than what was observed, which can be accounted for by an increase in the grain boundary volume as the grain size was strongly reduced upon hydrogenation.

It would be very interesting to perform NR during multiple cycles. As the segregation step would only occur in the first cycle, volume expansion should be instantaneous, while retaining the rapid hydrogen diffusion. As phase separation requires diffusion of metal atoms, this would also explain the observed improvement of the kinetics after the first cycle.

In summary, the effect of alloying Mg with transition metals on hydriding kinetics was studied with Neutron Reflectometry for the first time by contrasting pure Mg with an Mg–Cr–V alloy. Combined NR and XRD analysis showed that Cr and V segregate from Mg in the first hydrogenation cycle, forming a percolating network through Mg, evidenced by the strongly reduced grain size of MgH₂ compared to pure Mg. Formation of a blocking MgD₂ layer was prevented and deuteration proceeded nearly homogeneously through an abundance of heterogeneous nucleation sites. Enhanced deuterium diffusion was confirmed by the rapid deuteration of the bottom Ta layer.

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