

Dehydriding kinetics of a Mg–9.5 wt% V sample studied by high pressure differential scanning calorimetry

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Abstract

The effect of the additive V on the rate of hydrogen desorption from MgH₂ is investigated using high-pressure differential scanning calorimetry (HP-DSC). The HP-DSC data obtained at different temperatures were analysed in terms of the nucleation and growth of the Mg phase within the hydride matrix and the subsequent movement of the phase boundary. Activation energies (E_A) obtained for the different steps show that the rate determining step is very much dependent on the conditions of dehydriding. The high value of E_A found (~600 kJ mol⁻¹ H) for the nucleation step suggests that the V inhibits nucleation of the α -Mg from the hydrided Mg–9.5 wt% V composite sample. This has been attributed to the precipitation of vanadium in the MgH₂ matrix creating accommodation strains, leading to dislocations around the vanadium particles. These can then act as sinks for the hydrogen thereby increasing the activation energy for nucleation of hydrogen.

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1. Introduction

Despite having a very high hydrogen capacity of 7.6 wt%, MgH₂ suffers from poor dehydriding kinetics, a high hydride stability and very poor cycling stability. The drive to develop more suitable Mg-composite materials and hence overcome some of these limitations has been extensive through the use of metals [1,2], non-metals [1,3] and intermetallics [4–9]. Depending on the method of preparation of these composite materials, an enhancement in both the thermodynamic properties and kinetics, with respect to pure Mg, have been reported and these have been associated with specific physical processes which occur during the preparation. For example, during the mechanical alloying of Mg with Ni, a new intermetallic phase (Mg₂Ni) with a correspondingly lower plateau temperature but also lower hydride content (3.6 wt%) can result. Furthermore, the presence of Ni acts as a strong catalyst for the dissociation of hydrogen.

In this work, the physical vapour deposition (PVD) [10]

technique, was employed in the preparation of the Mg–V composite studied. It is worthwhile noting that the hydriding and dehydriding of Mg involves several steps [11,12]. The experimental conditions determine which process becomes the rate determining step. Here, we concentrated on investigating the dehydriding step using the technique of high-pressure differential scanning calorimetry (HP-DSC). The experiments, carried out under isothermal conditions for constant loadings should enable the delineation between some of the various steps involved in the dehydriding process. A comparison of our data to other similar work, such as that of Liang et al. [13] on Mg composites including Mg–V and that of Bohmhammel et al. [14] for Mg would also be helpful in the analysis.

2. Experimental

The Mg+9.5 wt% V samples were prepared by the physical vapour deposition (PVD) process. Here, the composites were obtained by co-evaporating magnesium from a boiler with V evaporated by electron beam from a rod feed. The composition of the vapour deposit was

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controlled by varying the temperature of the magnesium boiler. The evaporation rate of the V was maintained at a constant rate. The deposits were collected on an aluminium plate (200×200 mm) and thicknesses of up to 2 mm were produced. The HP-DSC employed was a Mettler-Toledo DSC HP27 controlled by a TC11 processor and interfaced to a personal computer. The experimental set-up has been described elsewhere [15]. The isothermal dehydriding experiments were only initiated once constant values of the absorption/desorption enthalpies were obtained during repeated temperature cycling at 17.5 bar H₂ pressure. Once these criteria had been met, a step change in the pressure in the HP-DSC from 17.5 bar to the required pressure (below the equilibrium pressure for that temperature) was carried out. The decomposition of the metal hydride thus occurred spontaneously on pressure reduction and the heat flow corresponding to the hydrogen desorption was recorded by the HP-DSC.

3. Results and discussion

As has been well documented [12], the intrinsic processes concerned with the dehydriding reaction are: (i) the phase transformation from hydride into an α -solid solution and hydrogen atoms. (This implies the formation of nuclei of magnesium metal within the bulk magnesium hydride phase, followed by α -solid phase growth); (ii) the diffusion of hydrogen atoms through the growing layer of the α -solid solution; (iii) the transition of hydrogen atoms from their absorbed state into their chemisorbed state; and (iv) the associative chemisorption of hydrogen atoms on the surface of the metal. Stander [11] examined in particular the first step which includes nucleation and phase growth. In the case of instantaneous nucleation of the Mg metal at sites within the magnesium hydride matrix, the rate of

decomposition will be determined by movement of the Mg–MgH₂ phase boundary. In this instance and assuming that the boundary progresses at a constant velocity within the matrix, the fractional decomposition, α , can be related to the reaction time by the relation:

$$1 - (1 - \alpha)^n = k_1 t \quad (1)$$

where k_1 is the rate constant for the process and n depends on the shape of the interface. Here, a value of 1/2 was taken for n since the tetragonal structure of the hydride and the hexagonal close-packed structure of the Mg metal gives rise to a cylindrical interface [11]. On the other hand, the growth of the nuclei could be progressive rather than instantaneous and in this instance and following the work of Avrami [16], the relevant expression is:

$$(-\ln(1 - \alpha))^{\frac{1}{2}} = k_2 t \quad (2)$$

Integration of the HP-DSC desorption curves yields the enthalpy associated with the process and so permits the calculation of the reacted fraction during the dehydriding process as a function of time. Fig. 1 shows the plot of the dehydrided fraction versus time for the Mg–9.5 wt% V composite at a temperature of 372 °C as a result of a pressure step from 17.5 to 8.1 bar. Fig. 2 shows the plot according to Eq. (1) over the dehydrided fraction range of 0.22 to 0.82 for the movement of the α -Mg/MgH₂ phase boundary at 372 °C following the pressure step. An excellent fit ($R^2 > 0.99$) to Eq. (1) is obtained allowing us to conclude that over this reacted fraction range, it is the movement of the phase boundary which is the rate-determining step. By carrying out similar evaluations on data obtained over the temperature region 362–380 °C, the activation energy for this process could be deduced from an Arrhenius plot as $\sim 530 \pm 30$ kJ mol⁻¹ H. The rather narrow temperature region in which reliable data could be

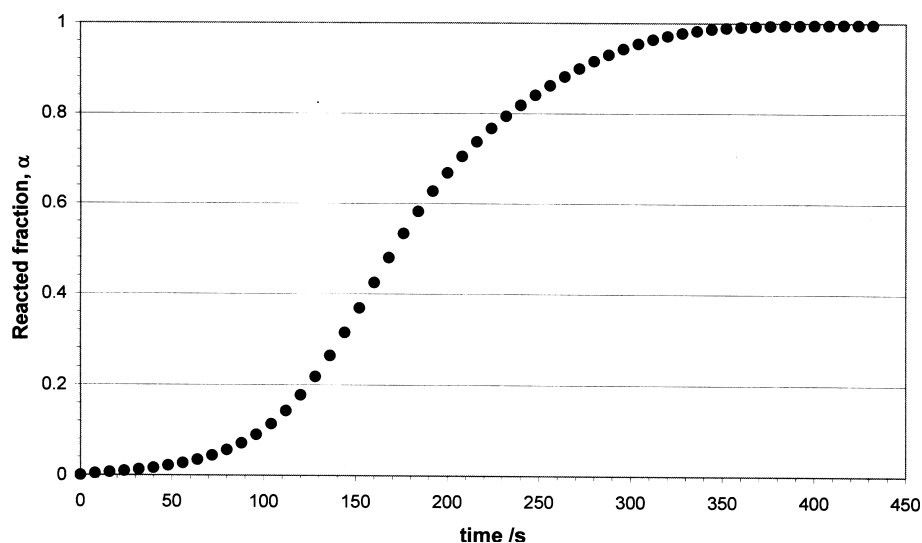


Fig. 1. Reacted fraction as a function of time for dehydriding of Mg–9.5 wt% V composite after a pressure step from 17.5 to 8.1 bar at 372 °C.

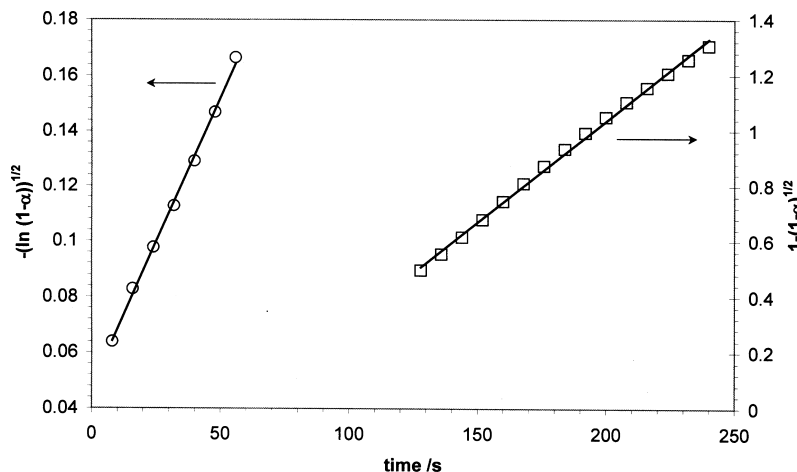


Fig. 2. Plots of $1-(1-\alpha)^{1/2}$ and $(-\ln(1-\alpha))^{1/2}$ versus time corresponding to the α -Mg phase boundary growth and, nucleation/growth of the α -Mg solid solution within the hydrided Mg–V matrix, respectively, following the pressure step from 17.5 to 8.1 bar at 372 °C.

acquired by the HP-DSC is a consequence of the relatively small pressure difference in the experiments here and the temperature required to enable hydrogen absorption/desorption at this pressure.

On the other hand, by examining the data at a shorter time scale and so over a much lower reacted fraction range, information relevant to the nucleation stage of the α -Mg could be determined through the use of Eq. (2). Fig. 2 also shows the plot of Eq. (2) for the same experimental data as for Fig. 1. Again here, an excellent correlation is obtained signifying that the dehydriding process is governed by nucleation in these early stages. Once again, the activation energy can be obtained from the Arrhenius plot (Fig. 3) and here, the value for E_A found is $\sim 600 \text{ kJ mol}^{-1}$. This value is an order of magnitude higher than that obtained by Liang et al. for hydrogen desorption of MgH_2 -V composites recorded using an automatic Sieverts apparatus [13]. Indeed, it is even some five to six times

higher than the value found in the literature [11,14,17,18] for desorption from pure MgH_2 . A key difference though between our samples and those used by the previous workers is that our sample was produced by the PVD process. The samples of Liang et al. [13] for example were prepared by milling MgH_2 with vanadium under an argon atmosphere. No details of the vanadium distribution in that sample are given but it is unlikely that in the mechanical alloying preparation method, this distribution will be as uniform as that obtained by the PVD method. Furthermore, surface studies of the PVD Mg–V composite revealed that vanadium did not take part in the oxide film due to the high affinity for oxygen by magnesium [19]. Thus, the production of vanadium oxide is highly unlikely, especially in the bulk and the catalytic effect of V towards hydrogen chemisorption should remain high.

No ready explanation can be found as to why the dehydriding of the Mg–V composite appears much slower

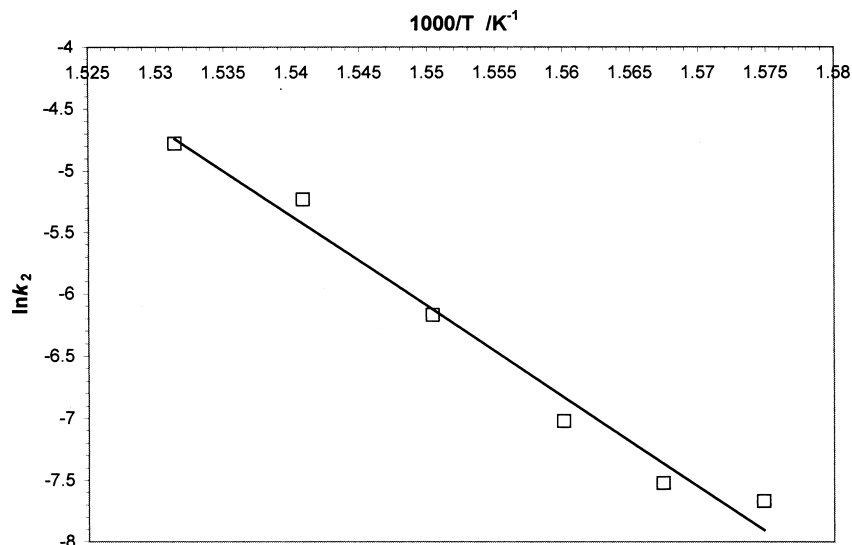


Fig. 3. Arrhenius plot for the nucleation/growth stage of the dehydriding process for a pressure step from 17.5 to 8.1 bar.

than that for MgH_2 alone. It must be remembered though that V is capable of being hydrided on its own. VH_2 has a plateau pressure of 1 bar at only 12 °C. The formation of the vanadium hydride during mechanical milling with MgH_2 , as noted above, could well protect the V from oxidation and assist in the transfer of the hydrogen to the MgH_2 during subsequent hydriding cycles. In our PVD samples, this may not be occurring. Because of the negligible solid solubility of vanadium in Mg, it is expected that thermal cycling would inevitably result in the precipitation of vanadium as clusters in the matrix. Evidence for such precipitation in Mg–V PVD deposits has been previously observed [19]. The PVD process route thus generates a solid solution of V in a Mg matrix. On heat treatment to 500 °C, nanoscale V precipitates are formed throughout the microstructure. As the growth of the precipitates is limited by the diffusion of V within the matrix, the structure is thus pure V nanocrystallites distributed throughout the Mg matrix. Elemental vanadium has the disordered BCC structure with octahedral and tetrahedral voids available for the storage of hydrogen. In the practical H storage limit of VH_2 the metal structure transforms to the FCC cubic structure to provide enough tetrahedral sites [20]. With extensive hydriding/dehydriding cycling, there are significant degradations in the plateau pressure, slope, hysteresis and hydrogen storage capacity [21]. This is attributed to unusually large anisotropic plastic strains and crystal disorder that occur during cycling. An additional result is that significant H becomes ‘trapped’ and unavailable for cyclic recovery. The precipitation of vanadium in the MgH_2 matrix is thus bound to create accommodation strains because of the changes in lattice parameter of the matrix alloy as it rejects vanadium. This can lead to the creation of dislocations around the vanadium particles, which can then act as sinks for the hydrogen thereby increasing the activation energy for nucleation of hydrogen.

4. Conclusions

The effect of the additive V on the rate of hydrogen desorption from MgH_2 has been investigated using HP-DSC. The data obtained at different temperatures were analysed in terms of the nucleation and growth of the α -Mg phase within the hydride matrix and the subsequent growth of the phase boundary. The rate determining step is

very much dependent on the conditions of dehydriding. The high value of E_A found ($\sim 600 \text{ kJ mol}^{-1} \text{ H}$) for the nucleation step clearly indicates that the V inhibits nucleation of the α -Mg from the hydride phase of the Mg–9.5 wt% V composite. This has been attributed to strain produced in the MgH_2 matrix by the precipitation of vanadium, leading to dislocations around the vanadium particles. These dislocations act as sinks for the hydrogen thereby greatly increasing the activation energy for α -Mg formation.

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