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The effect of novel processing on hydrogen uptake in FeTi- and magnesium-based alloys

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Abstract

This paper discusses the production and initial evaluation of hydrogen storage alloys produced by physical vapour deposition (PVD) and mechanical alloying (MA). PVD is usually associated with the production of thin films and coatings. However, DERA Farnborough have developed a high rate vapour condensation process to produce bulk deposits, in some cases up to 44 mm thick. Vapour condensation using electron beam evaporation produces the ultimate in cooling rates with extended solid solubility and refinement of microstructure, which produce enhanced physical and mechanical properties. MA is a complimentary technique for processing hydrogen storage materials which has been developed within DERA over the past 3 years. These techniques have been applied to Mg and FeTi alloy systems and it is shown that both methods greatly enhance the amount of hydrogen uptake and the ease of activation.

Keywords: Mechanical alloying; Physical vapour deposition; Hydrogen storage; Thermal analysis

1. Introduction

The use of metal hydrides as hydrogen storage devices stems from the discovery by Thomas Graham in 1866 [1] of the ability of palladium to absorb large amounts of hydrogen (H:Pd=1). Since then, many more metals and alloys have been found to possess a similar ability although not the same ease of incorporating of hydrogen within their lattice. Mg and Mg-based alloys, for example, have considerable potential for reversible hydrogen storage [2,3] with a 7.6 wt% capacity for MgH_2, but this material has limited applications because of its very high stability. The FeTi system has among its advantages also a high H:M ratio (~1) as well as a high abundance of the component materials. However, special activation procedures have to be followed before this alloy can be employed for hydrogen storage [4,5]. These two systems, i.e. pure Mg and FeTi alloys, will be discussed in this paper where similar compositions have been made by physical vapour deposition (PVD) and mechanical alloying (MA). The hydrogen storage capabilities of both the PVD and MA materials will be compared to commercially available FeTi hydrogen storage powder (Johnson–Matthey) and pure Mg ingot (Norsk Hydro).

2. Experimental

DERA has developed a mechanical alloying route for the production of solid solution powders from both elemental and alloyed feedstock. A high energy milling system operated in an inert atmosphere was employed to generate the MA material for hydrogen storage evaluation. A unique bulk alloy production technique using physical vapour deposition (PVD) was also employed. In this technique, the vapour condensation process developed overcomes many of the limitations of molten metal processing. For example, novel alloys, impossible to produce by other techniques can readily be produced and alloys can be generated with extended solid solubilities and ultra-fine microstructures. The vapour distillation also purifies the alloy through differences in vapour pressure between impurity and alloying elements.

The basic design of the PVD equipment is shown in Fig. 1. The whole set-up is enclosed in a vacuum chamber. To prepare the FeTi alloy, a rod of the required composition is made by arc melting the constituent elements. This alloy is

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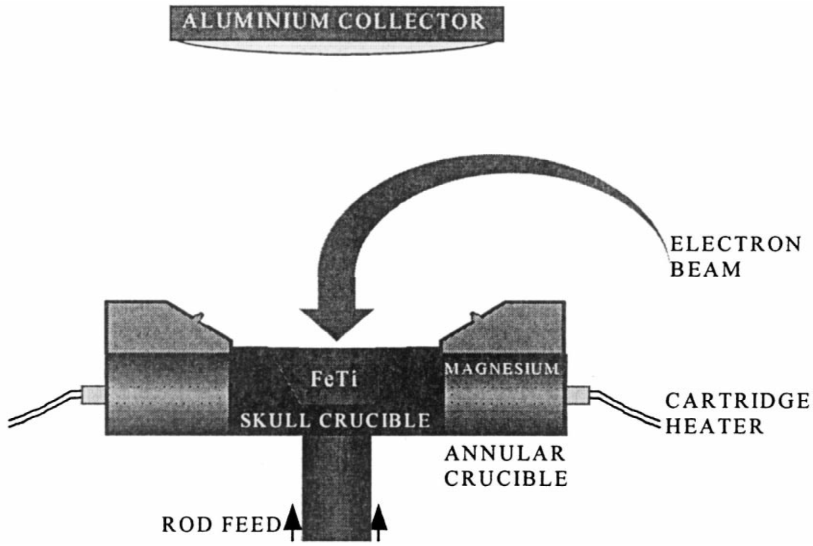

Fig. 1. Schematic diagram of vapour condensation process.

then evaporated by the electron beam gun and the vapour condenses onto a cooled collector plate. For pure magnesium, an annular steel boiler heated by radiant heaters is employed. Magnesium vapour is directed towards the collector plate by a number of nozzles in the boiler. The temperature of the collector is set at a predetermined value to control the porosity of the deposit. An optimisation of this temperature is required since lower temperatures favour solid solutions, whilst higher temperatures reduce the porosity. The versatility of this equipment enables many different alloy compositions to be prepared.

The hydrogen storage capability of the systems produced were investigated by the thermal analytical technique of high-pressure differential scanning calorimetry (HP-DSC). The HP-DSC (Mettler-Toledo DSC 27HP and TC-11 interface unit) was fitted with a Brooks Instrument Pressure Controller (Model 5866) which stabilised the pressure inside the cell. The system has been designed to allow samples to be loaded with hydrogen (5.5 Grade, Air Products) under elevated temperatures (~500°C) and pressures (60 bar) and then sequentially desorbed by applying a heating ramp. The amount of hydrogen absorbed and desorbed can then be related to the enthalpy (ΔH) values recorded during these events. In the present experiments, a pressure of 30 bar was used throughout. Aluminium pans were normally employed as sample holders and as reference in these experiments. However, in instances where the possibility of reaction between the Mg sample and the Al pans existed, platinum pans were used. Thermogravimetric measurements were conducted on a Perkin-Elmer TGA 7 thermogravimetric analyser under a purge of argon gas.

Further investigations of the hydrogen storage capacity was carried out using the method of pressure–composition isotherm studies. A rig was designed following the principles described by Friedlmeier and Bolcich [6] and the alloys were charged and discharged by increasing or decreasing the pressure of hydrogen in the system, respectively. In this way pressure–composition isotherms were obtained.

3. Results and discussions

3.1. Magnesium

The testing regime used to assess the hydrogen storage capability of these alloys is shown in Table 1.

The commercial Mg was given 10 cycles, and although the sample underwent hydriding almost immediately, with a gradual increase in hydrogen uptake on subsequent cycling, the enthalpies of dehydriding and hydriding remained low (see Table 2), signifying very little hydriding was taking place. With no significant improvement after 10 cycles, the test was halted. On the other hand, both the PVD and MA magnesium exhibited immediate and signifi-

Table 1
Test conditions used to monitor hydriding/dehydriding of magnesium (heating rate = 10 K min^{-1})

	Commercial Mg	PVD Mg	MA Mg
Cycling conditions	30→500→30°C	30→500→30°C	30→500→30°C
Number of cycles	10	5	6
Hydriding temp. (°C)	400	405	408
Dehydriding temp. (°C)	466	450	442

Table 2
Enthalpy (ΔH) values on temperature cycling in 30 bar H_2 for magnesium samples prepared by different methods

Cycle	Commercial		PVD		MA	
	Dehydriding, ΔH (J g^{-1})	Hydriding, ΔH (J g^{-1})	Dehydriding, ΔH (J g^{-1})	Hydriding, ΔH (J g^{-1})	Dehydriding, ΔH (J g^{-1})	Hydriding, ΔH (J g^{-1})
1	Too low to register		–	1042.6	–	213.8
2	Too low to register		882.7	1011.2	265.8	680.7
3	Too low to register		920.2	896.5	626.9	813.5
4	1.9	3.4	924.8	884.0	772.6	832.1
5	3.2	7.2	818.9	795.6	819.8	796.9
6	5.4	11.2			805.0	749.0
7	8.0	–				
8	4.2	14.1				
9	8.0	16.9				
10	12.7	16.6				

cant hydrogen uptake. These results are in agreement with previous findings [7,8] that particle size, morphology, purity and degree of surface oxidation all have an influence on the kinetics of hydrogen absorption by Mg. The figures do not appear to show stability after five cycles and it is possible that further cycling would improve the hydrogen storage capacity for the MA alloy, although for the PVD alloy, a decrease in the enthalpy for absorption was recorded with cycling number. The final HP-DSC traces for the differently prepared material are shown in Fig. 2.

3.2. Iron/titanium

The same testing regime as above was used for the FeTi samples. With this method, it was found that the commercial FeTi powder was not activated and no hydrogen uptake was possible. The results for the thermal cycling in 30 bar H_2 for PVD FeTi are shown in Fig. 3. The first heating cycle showed no desorption, but a large exotherm at ca 326°C was observed which is attributed to the thermal annealing of the alloy. On cooling, a small exotherm at ca 119°C shows that some hydrogen uptake occurs even on this first cycle. A broad desorption endotherm at ~157°C is then found on the next heating cycle. Both desorption and absorption enthalpies show some deviation over the five cycles examined (28.5 ± 2 and 54.8 ± 5 J g^{-1}, respectively), but it is clear from the thermogravimetric data shown in the last sub-figure that ~0.8 wt% loading was achieved even after these few cycles. Volumetric hydrogen sorption experiments on FeTi

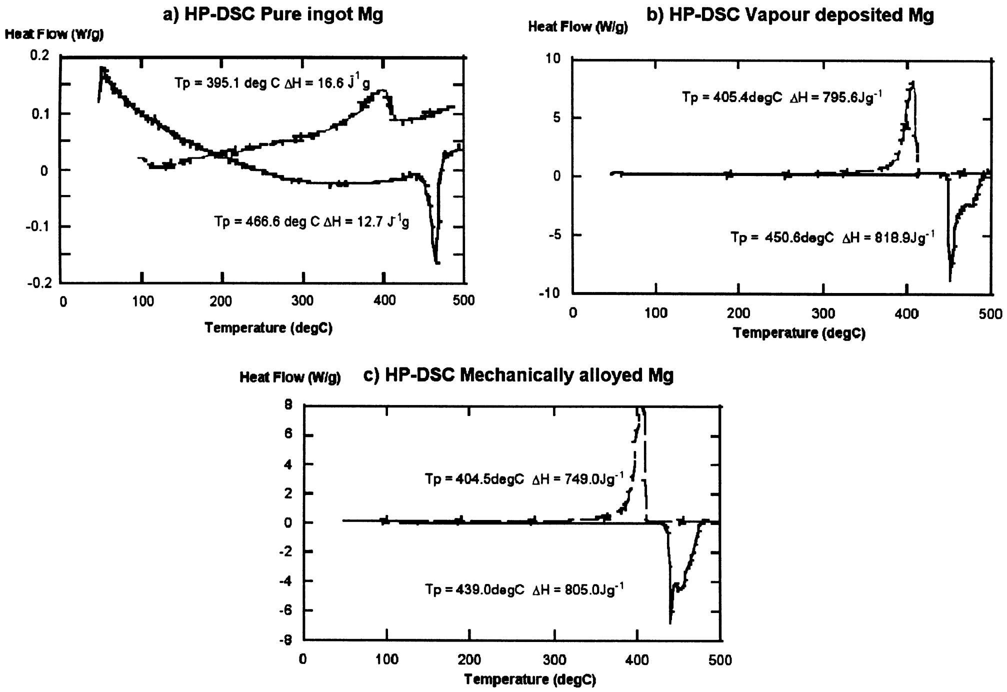

Fig. 2. Comparison of heat flows during hydrogen absorption/desorption for magnesium samples prepared by different methods. (a) Ingot, 10th cycle; (b) PVD, 5th cycle; and (c) MA, 6th cycle.

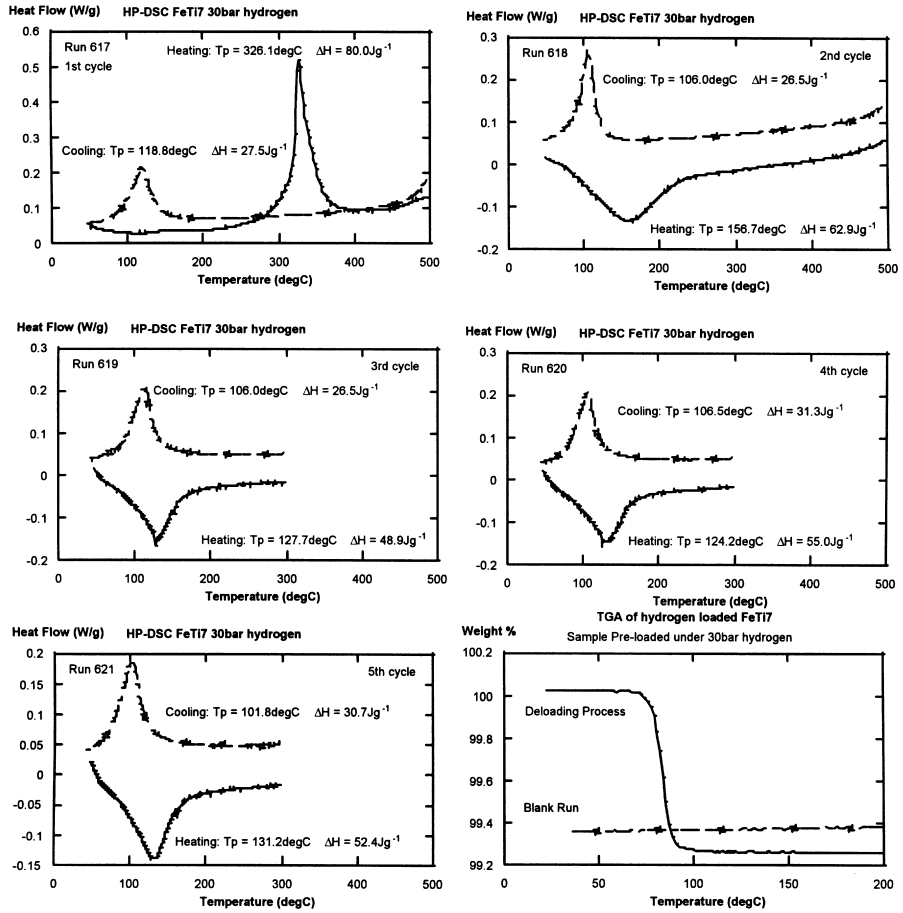

Fig. 3. Comparison of heat flows during hydrogen absorption/desorption for magnesium samples. The last figure shows data from TGA analysis after the fifth thermal cycle.

were also carried out and, under the conditions employed, neither the initial commercial FeTi alloy nor the two others that were bought in could be made to store hydrogen even after extreme activation procedures (500°C and 65 bar H_2). Following activation, the PVD and MA alloys studied here registered absorption capacities of 1.2 and 1.4 wt% hydrogen with the desorption capacities slightly (0.2 wt%) lower. The desorption pressure–composition isotherm measured at 50°C for a MA FeTi sample is shown in Fig. 4. The well-defined plateau region is typical of hydrogen storage alloys and is in good agreement with the work of Reilly and Wiswall [9].

Although the storage capacity achieved for FeTi alloys prepared by PVD and MA was slightly lower than that quoted for commercial products (1.2 wt% here as compared to 1.8 wt%) the ease of activation was greatly improved. The microstructure also plays a determining role in the level of hydriding obtained. The development of new un-conventional fabrication methods has led to the production of nanocrystalline materials for use as hydrogen storage materials. Nanocrystalline materials show enhanced absorption and desorption kinetics, even at relatively low temperatures, coupled with a reduction in the activation process. Polycrystalline FeTi, for example, requires a rigorous activation process involving heating up to 450°C under vacuum and subsequent exposure to a high pressure of hydrogen several times in succession before noticeable hydriding occurs. This is in contrast to MA nanocrystalline FeTi which requires a single and much simpler activation process to induce hydriding. The im-

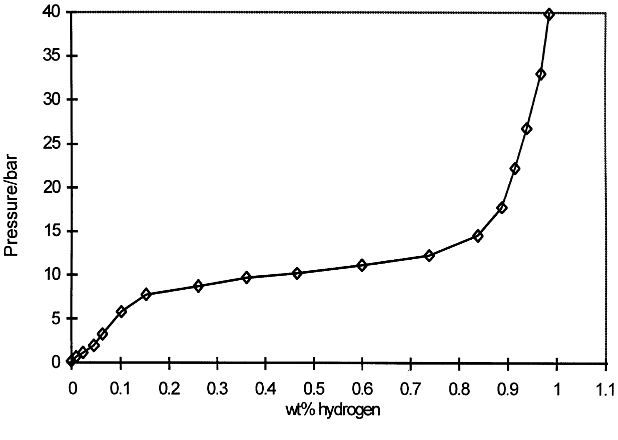

Fig. 4. MA FeTi desorption: pressure–composition isotherm at 50°C.

provement in properties is attributed to the availability of well-established diffusion paths for hydrogen atoms along the numerous grain boundaries and hydrogen atoms preferentially dissolving into the inter-grain region [10].

The lower than expected hydrogen capacity in the novel processed material may be because the FeTi samples are only exhibiting one of two possible hydride states. Traditional iron titanium has two distinct hydriding reactions:

$$2.13\ \underset{\alpha\text{-hydride}}{\mathrm{FeTiH}_{0.1}} + \mathrm{H}_2 \Leftrightarrow 2.13\ \underset{\beta\text{-hydride}}{\mathrm{FeTiH}_{1.04}}$$

$$2.20\ \underset{\beta\text{-hydride}}{\mathrm{FeTiH}_{1.04}} + \mathrm{H}_2 \Leftrightarrow 2.20\ \underset{\gamma\text{-hydride}}{\mathrm{FeTiH}_{1.95}}$$

Recent work [11] on ball-milled FeTi suggests that after ball milling the iron titanium can only be converted to the β-hydride and not to the γ-hydride. In addition, exposure to the air may cause contamination of the material and reduction of active surface area. This is especially true for magnesium-containing alloys. To reduce exposure to air, an inert collector system has been built to allow vapour-deposited samples to be removed from the collector plate and transferred to an inert atmosphere without exposure to the air. The MA process is already fully inert, but all material detailed in this paper have had considerable exposure to air. It is expected though that during the activation procedure under the reducing action of the high pressure hydrogen gas, the deleterious effect of these surface oxide species would be removed or greatly minimised.

4. Conclusions

The influence of processing on the kinetics of hydriding is clearly demonstrated by the comparison between Mg ingot and Mg produced by MA or PVD. The material processed by MA or PVD is more readily activated and has a larger hydrogen storage capacity than the pure ingot. The large ΔH values measured in the HP-DSC for the latter two materials were unexpected and these material will be further investigated using volumetric techniques and thermogravimetric analysis to determine the actual hydrogen storage capacity. It is clear, nevertheless, that both systems are capable of reversibly storing appreciable amounts of hydrogen. A direct comparison of the ΔH values of Mg and FeTi prepared by PVD shows that the degree of loading achieved are $\mathrm{MgH}_{0.52}$ and $\mathrm{FeTiH}_{0.2}$, noting that the enthalpy of formation of magnesium hydride is over twice that of the formation of iron titanium hydride (ΔH_f $\mathrm{MgH}_2 = -80$ kJ mol^{-1} H_2; ΔH_f FeTiH $= -30$ kJ mol^{-1} H_2). The temperature of desorption does not seem to be significantly affected by the process route. Future work is concentrating on the inert collecting system and development of new alloys based on novel magnesium systems. The eventual aim is to develop a low-temperature high-capacity hydrogen storage metal hydride.

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