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Competing stabilisation mechanisms in Mg_2NiH_4

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Abstract

By using three different Mg_2Ni alloys to synthesise Mg_2NiH_4 an additional stabilisation mechanism of this system has been identified. It has been known for some time that the stacking faults at unit cell level in the lattice, microtwinning, stabilise this hydride thermodynamically, but the results in this study also reveal that the addition of free magnesium from the casting of the starting alloys have a similar stabilising effect on the hydride. It is also clear that these two stabilisation mechanisms are connected to each other, i.e. the microtwinning in Mg_2NiH_4 is dependent not only on the thermal history of the sample but also of the amount of free magnesium added at the casting of the Mg_2Ni alloy. The extra magnesium acts as a stabilising dopant to the Mg_2NiH_4 system and in addition to this gives interesting colour effects of the low-temperature phase of Mg_2NiH_4.

Keywords: Mg_2NiH_4; Alloys; Stabilisation mechanisms; Metal hydride

1. Introduction

Since 1968 when Reilly and Wiswall [1] discovered the reversible hydrogen absorption ability of the alloy Mg_2Ni to form the ternary hydride Mg_2NiH_4, its hydriding–dehydriding, structural, electric, thermal and kinetic properties have been investigated by many research groups. During the years Mg_2NiH_4 has continued to surprise the researchers by exhibiting structural changes, colour [2] and resistivity anomalies [3], seemingly unpredictably dependent on sample preparation and sample history.

Mg_2NiH_4 has been regarded as a promising metal hydride for hydrogen storage and for increasing the negative electrode capacity in the nickel metal hydride (NiMH) batteries. However, under normal conditions Mg_2NiH_4 is too stable, i.e. at room temperature the equilibrium pressure is so low that Mg_2NiH_4 practically does not desorb hydrogen. Therefore it is essential to decrease the stability of Mg_2NiH_4 to produce a suitable material for practical hydrogen storage.

Below 510 K, Mg_2NiH_4 exhibits a monoclinic distorted low-temperature modification (LT) of a cubic high-temperature phase (HT), where magnesium ions form a cube around zerovalent NiH_4-complexes in an antifluorite arrangement. In the HT phase the hydrogen atoms perform a rapid reorientational motion around the central nickel atom [4]. In the LT phase this motion is ‘frozen’ and an ordered arrangement of slightly distorted tetrahedral NiH_4-complexes is observed by neutron diffraction [5]. In addition to this a frequently occurring stacking fault or microtwinning on unit cell level is introduced into the lattice [5,6]. If the microtwinning is suppressed the stability of the hydride is decreased, making it more practical for hydrogen storage [7].

The stability of a series of related zerovalent palladium complexes in Na_2PdH_2, $NaBaPdH_3$ and Ba_2PdH_4 could be explained by a substantial bonding interaction between the complexes and the electropositive counter ion matrix as an alternative to conventional ‘back bonding’ [8–10]. By adopting a similar approach to Mg_2NiH_4, containing a nickel analogue of the PdH_4-complex, we can better understand the peculiarities of Mg_2NiH_4 and suggest ways to increase the hydrogen release pressure from Mg_2NiH_4.

2. Experimental

Three different Mg_2Ni alloys were used for synthesising the Mg_2NiH_4; Mg_2Ni prepared by bulk mechanical alloying (BMA) from Mitsui Mining and Smelting in Japan [11] (marked **A** in Fig. 1) and two Mg_2Ni alloys prepared by conventional casting techniques, supplied from JMC in

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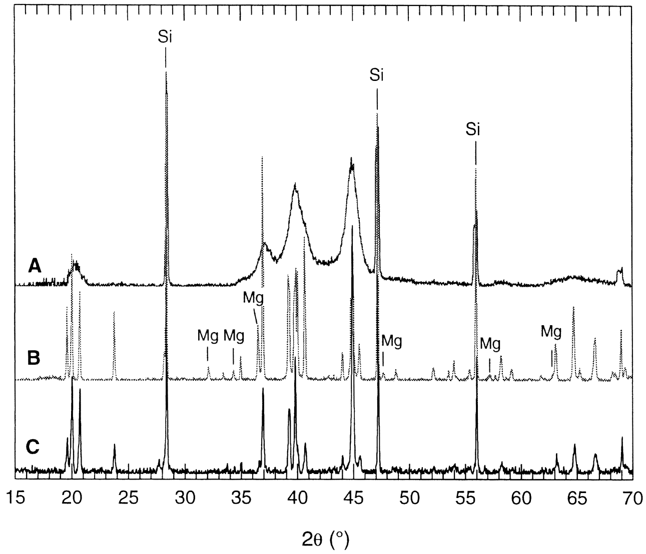

Fig. 1. X-ray diffraction profiles of the three different starting alloys used in the experiments. The profile marked **A** is prepared by a bulk mechanical alloying method, while the profiles marked **B** and **C** are Mg_2Ni prepared by conventional casting techniques. Silicon has been used as internal standard.

Japan (**B**) and by MPD-Technology Corp. (**C**). The two latter alloys, especially the alloy marked **B**, contain a slight excess of free magnesium metal to prevent the formation of $MgNi_2$ during the preparation.

The Mg_2Ni alloys were activated at 620 K by absorption and desorption of hydrogen, using a pressure of 50 bar. The low-temperature phase (LT) with microtwinning (LT2) was obtained by cooling the high-temperature phase (HT) of Mg_2NiH_4 to room temperature. To obtain the LT phase without microtwinning (LT1), the sample was first dehydrided with a vacuum pump at 620 K and the temperature was then lowered to 400 K for 1 or 2 days. Hydrogen was then carefully added at a pressure of 50 bar and the temperature was raised to 450 K, which is below the transition temperature (510 K) between the HT and LT phases. The sample was then kept at this temperature at 50 bar for two days. All samples were handled under argon atmosphere in a glove-box with less than 1 ppm O_2 and H_2O.

The samples were investigated by taking their X-ray powder photographs in a Guinier–Hägg focusing camera of 40 mm diameter, using monochromatised Cu Kα1 radiation (λ=1.5405981 Å). Si (a=5.430879 Å at 25°C) was added as an internal standard to increase the accuracy of the 2θ-scale. The photographs obtained were measured in a LS 18 film scanner [12]. The program SCANPI [13] was used to evaluate the photographs and the program PIRUM [14] was used to index the patterns.

To examine the composition of the starting materials the samples were investigated in the scanning electron microscope (SEM) in combination with EDX analysis, JEOL 820/LINK AN 10000, operating at 20 kV. The EDX results were based on the Mg (K) and Ni (K, L) lines in the spectra.

3. Results and discussion

3.1. Effect of Mg addition to the alloy

The amount of microtwinning in the LT phase of Mg_2NiH_4 is dependent on the thermal history of the sample but also, as the present work shows, to unintentionally added Mg from the casting of the alloy. According to the phase diagram [15] a single phase of the Mg_2Ni alloy can not be obtained from solidification of the Mg_2Ni melt. To avoid the co-precipitation of $MgNi_2$ the casting of Mg_2Ni is done with an excess of Mg, which means that 'Mg_2Ni alloys' so far investigated contain a small amount of free magnesium, such as for example the alloys **B** and **C** in this study. The addition of extra Mg and formation of $MgNi_2$ can be avoided by preparing the alloy by bulk mechanical alloying (BMA). The composition of the Mg_2Ni alloys can thus vary, which is also the case in this study. The results from the EDX analyses of alloys used can be seen in Table 1.

Fig. 2 shows X-ray diffraction patterns of LT2-Mg_2NiH_4 synthesised from the three different alloys. The peak at 2θ=23.7° (marked with an arrow in Fig. 2) is attributed to microtwinning [5,6] in the hydride lattice. The varying intensity of this peak is clearly correlated to the different amounts of Mg in the starting alloys **A**, **B** and **C**. When using alloy **A** (prepared by BMA) to synthesise the LT2 form of Mg_2NiH_4, the peak intensity is increased, which we presently assume to correspond to an increased amount of microtwinning in the hydride lattice. When using alloy **B** that contains the highest amount of extra Mg, the microtwinning is much less abundant than for alloy **A** and **C**. The hydrides made from alloy **B** and **C** also contain a slight amount of MgH_2, due to the extra amount of free Mg in those starting alloys.

The colour of LT2-Mg_2NiH_4 made from alloy **B** and **C** is orange, which is typical for the hydride [1]. However, when **A** is used as starting alloy the orange colour does not appear and the sample is left brown–greyish. If extra MgH_2 is ground together with **A**, or the hydride synthesised from alloy **A**, the amount of microtwinning will be reduced and the LT2-Mg_2NiH_4 becomes brightly orange. This colour effect has also been observed when

Table 1
Results from EDX analyses show that the content of Mg and Ni varies in the alloys used in the study

Alloy	Mg (atom%)	Ni (atom%)	Ratio Mg:Ni
A	61.6±2.1	38.4±2.1	1.6±0.1:1
B	68.0±6.2	32.0±6.2	2.2±0.7:1
C	64.4±4.4	35.6±4.4	1.9±0.4:1

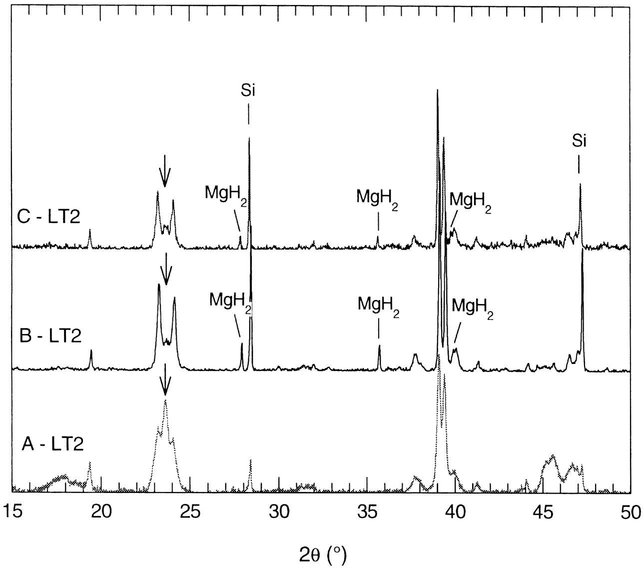

Fig. 2. X-ray diffraction profiles of the LT2-Mg_2NiH_4 synthesised from alloy **A**, **B** and **C**. Note the difference in intensity of the peak marked with an arrow at $2\theta=23.7°$.

other earth alkaline metal hydrides as CaH_2, SrH_2 and BaH_2 were added to the alloy, but not to the same extent as for MgH_2.

3.2. Phase transition

When heating the LT2-Mg_2NiH_4 synthesised from **B** and **C** across the LT→HT transition at 510 K the orange colour abruptly disappears but reappears as it is cooled again. The same colour change can only be observed for the hydride synthesised from **A** after MgH_2 has been added to the sample. This observation excludes that the orange colour is from MgH_2 only and reflects how the NiH_4-complex uses different available routes for obtaining stability.

4. Conclusions

Destabilisation of Mg_2NiH_4 can be attained by eliminating the identified stabilisation mechanisms; microtwinning and the extra Mg from the starting material, which acts as a dopant to this system. These stabilisation mechanisms are competing with each other, but the details about this behaviour still are unclear. To avoid the stabilising effects of Mg_2NiH_4 the starting alloy should be prepared by bulk mechanical alloying and the synthesis should be made at lower temperatures.

References

[1] J.J. Reilly, R.H. Wiswall Jr., Inorg. Chem. 7 (1968) 2254.
[2] E. Rönnebro, Doctoral Dissertation, Stockholm University, 1999.
[3] Z. Gavra, G. Kimmel, Y. Gefen, M.H. Mintz, J. Appl. Phys. 57 (1985) 4548.
[4] D. Noréus, L.G. Olsson, J. Chem. Phys. 78 (1983) 2419.
[5] P. Zolliker, K. Yvon, C.H. Baerlocher, J. Less-Common Metals 15 (1986) 65.
[6] D. Noréus, L. Kihlborg, J. Less-Common Metals 123 (1986) 233.
[7] S.E. Guthrie, G.J. Thomas, D. Noréus, E. Rönnebro, Mater. Res. Soc. Symp. Proceed. 513 (1998) 93.
[8] M. Olofsson-Mårtensson, U. Häussermann, J. Tomkinson, D. Noréus, J. Am. Chem. Soc. 122 (2000) 6960.
[9] M. Olofsson, M. Kritikos, D. Noréus, Inorg. Chem. 37 (1998) 2900.
[10] M. Olofsson-Mårtensson, M. Kritikos, D. Noréus, J. Am. Chem. Soc. 121 (1999) 10908.
[11] T. Aizawa, T. Kuji, H. Nakano, J. Alloys Comp. 291 (1999) 248.
[12] K.E. Johansson, T. Palm, P.-E. Werner, J. Phys. E: Sci. Instrum. 13 (1980) 1289.
[13] P.-E. Werner, L. Eriksson, S. Salomé, SCANPI, a program for evaluating Guinier photographs, private communication.
[14] P.-E. Werner, Arkiv Kemi 31 (1969) 513.
[15] A.A. Nayeb-Hasheni, J.B. Clark, The Mg–Ni (magnesium–nickel) system, Bull. Alloy Phase Diagrams 6 (1985) 238.