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Attempts to improve Mg_2Ni hydrogen storage by aluminium addition

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Abstract

In an attempt to destabilize Mg_2NiH_4, the starting alloy, Mg_2Ni, was doped with aluminium by ball milling before hydrogenation. The structure of Mg_2NiH_4 is based on an electron-rich d^{10} $[NiH_4]$-complex stabilized by a Mg ion framework and from theoretical calculations it had been suggested that a further destabilization of the hydride could be obtained by substituting some Mg for Al. After hydrogenation, the structure, color and phase transition temperature of Mg_2NiH_4 was found to be affected by Al addition. The conventional monoclinic low-temperature (LT) structure of Mg_2NiH_4 was not observed by X-ray diffraction for $Mg_{2-x}Al_xNiH_4$, which instead could be indexed with a cubic unit cell, $a = 6.519$ Å, that is very close to the dynamically disordered, cubic, high-temperature (HT) phase of Mg_2NiH_4 ($a = 6.490$ Å). In contrast, the Al-doped Mg_2NiH_4 is stable at room temperature. Furthermore, the typical orange color of Mg_2NiH_4 was not observed and differential scanning calorimetric measurements (DSC) of the Al-containing hydride showed a 10 °C decrease in phase transition temperature. This is interpreted as a transition from a statically disordered *pseudo*-HT structure to the dynamically disordered HT phase. However, the monoclinic structure of the LT phase of Mg_2NiH_4 could again be observed at room temperature after 10 hydriding/dehydriding cycles, indicating that the Al-doping of Mg_2NiH_4 is counteracted by cycling and only has a temporary influence on the properties.

Keywords: Hydrogen storage materials; Mechanical alloying; X-ray diffraction; Calorimetry

1. Introduction

The compound Mg_2NiH_4 has attracted wide interest for being a promising hydrogen storage material and for its unusual structural and bonding properties. Mg_2NiH_4 forms readily by hydrogenating the alloy Mg_2Ni [1]. An intricate temperature polymorphism is observed, which comprises two different low-temperature forms (designated as LT1 and LT2 in the literature) and a high-temperature modification (HT) [2,3]. LT2 corresponds to a microtwinned variant of LT1 [4,5]. The cubic, dynamically ordered HT phase exists only above 235 °C, but recently a related structure, the *pseudo*-HT structure, was observed at room temperature [6]. Since the hydrogen desorption temperature is too high for convenient storage applications, intense research is trying to lower the thermal stability of Mg_2NiH_4. The microtwinning as well as the extra magnesium added to the starting alloy Mg_2Ni during fabrication has been found to stabilize the hydride [7,8]. The stabilizing mechanisms of the electron dense tetrahedral hydrido complexes in Mg_2NiH_4 were recently investigated by ab initio total energy calculations [9]. From the results, it was suggested that a lowered hydrogen desorption temperature could be achieved by introducing defects in the counterion matrix surrounding the tetrahedral $[NiH_4]^{4-}$ complexes, for example by substituting Mg for Al. Addition of aluminium to Mg_2NiH_4 has previously been investigated by Hirata et al. [10,11], and a slight decrease in stability of the hydride was then observed. In this study, an attempt to destabilize the complex has been made by doping the hydride lattice by ball milling Mg_2Ni together with small amounts of aluminium before hydrogenation. This was shown to have a profound effect on the phase transition temperature, color and structure of the hydride.

2. Experimental

Commercially pure Mg_2Ni (MPD Technology Corp.) and Al (Aldrich) were used as starting materials. Powder mixtures with chemical composition of $Mg_{2-x}Al_xNi$ ($x = 0.01$–0.04) were prepared and loaded into a stainless steel vial (25 ml) in an argon-filled glove box with less than 1

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ppm O_2 and H_2O. The initial mass of the powder mixture before ball milling was 5.0 g and the ball-to-mass weight ratio was 10:1. Ball milling was carried out in argon atmosphere, using a Spex 8000 ball mill. To minimize temperature increase during ball milling, the milling period of 15 min was alternated with an equal rest time. Total milling time was 10 h.

Hydrogenation of the ball milled mixtures was carried out at 350 °C at a hydrogen pressure of 50 bar for 2 days in a stainless steel reaction tube. Cycling of the sample was carried out by hydriding and dehydriding the sample 10 times.

Starting materials and products were investigated by X-ray powder diffraction with a Guinier-Hägg focusing camera of 40 mm diameter, using monochromatized Cu $K\alpha_1$ radiation (λ=1.5405980 Å). Si (a=5.430879 Å at 25 °C) was added as an internal standard. The photographs obtained were measured in an 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 with a JEOL 820/LINK AN 10000, operating at 20 kV. The EDX results were based on the Mg (*K*), Ni (*K, L*), Al (*K*) and Fe (*K*) lines in the spectra.

The thermal properties were studied by differential scanning calorimetry (DSC). The DSC curves were collected with a Perkin–Elmer Pyris 1 instrument at 5 °C/min in the temperature range 35–400 °C. Calibration of the instrument was carried out with tin (Sn) as standard. The samples were loaded in an argon-filled glove box and placed in hermetic stainless steel pans tightened with Cu-rings to avoid oxidation. Argon with a flow rate of 20 cm^3/min was used as purge gas. Empty stainless steel pans were used for baseline correction.

3. Results and discussion

Although up to 4 at.% Al was blended into the alloy mixtures before ball milling, the total Al-content never exceeded ≈1 at.% according to EDX results. In Table 1, the analyses of the alloy $Mg_{2-x}Al_xNi$ with initial x=0.03 is given together with the hydrided and cycled samples. A small amount of iron impurity, originating from the ball milling process, is observed. The XRD pattern of the ball milled alloy is shown in Fig. 1a. No peaks can be observed from Al. After hydriding, yielding the grayish product $Mg_{2-x}Al_xNiH_4$, neither the conventional monoclinic structure nor the orange color of LT2 Mg_2NiH_4 is observed. Instead the XRD pattern can be indexed as the cubic *pseudo*-HT structure [6] with a=6.519 Å (Fig. 1b). Probably the XRD results show an average structure between the previously published *pseudo*-HT structure (Fig. 1d) as well as the microtwinned monoclinic LT2 structure (Fig. 1e). It is difficult to separate the LT2 structure from the *pseudo*-HT structure due to peak overlap [6]. After 10 hydriding/dehydriding cycles, the structure of $Mg_{2-x}Al_xNiH_4$ partly reverts to the monoclinic LT Mg_2NiH_4 (Fig. 1c). Probably a small amount of Al, not detectable with XRD, is excluded from the lattice while cycling the sample. No color change is however observed, which would be expected if pure LT2 Mg_2NiH_4 was obtained and therefore it is suspected that some Al still remains in the lattice.

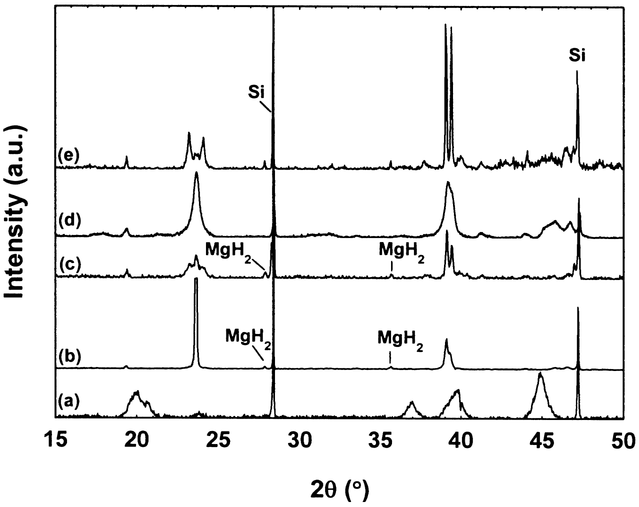

Fig. 1. X-ray diffraction pattern of (a) $Mg_{2-x}Al_xNi$ (x=0.03) after ball milling, (b) the hydrided alloy, $Mg_{2-x}Al_xNiH_4$, (c) the cycled hydride; (d) cubic *pseudo*-HT and (e) monoclinic, microtwinned LT2 Mg_2NiH_4 as references.

The thermal behavior of the Al-containing hydride differs from the non Al-containing LT Mg_2NiH_4. In Fig. 2, DSC curves of $Mg_{2-x}Al_xNiH_4$ (a), cycled $Mg_{2-x}Al_xNiH_4$ (b) and LT2 Mg_2NiH_4 (c) are shown. One endothermic peak is observed for all samples. For the Al-substituted hydride (Fig. 2a), the onset temperature of the phase transition is 224 °C. We attribute the peak to a transition from the statically disordered *pseudo*-HT structure to the

Table 1
Results from EDX analysis, based on eight analyses

Sample	Mg (at.%)	Ni (at.%)	Al (at.%)	Fe (at.%)
$Mg_{2-x}Al_xNi$ (x=0.03)	68.0±2.5	31.0±2.5	0.88±0.12	0.08±0.07
$Mg_{2-x}Al_xNiH_4$	70.4±6.0	28.7±6.2	0.80±0.24	0.11±0.05
Cycled $Mg_{2-x}Al_xNiH_4$	68.7±4.0	30.4±4.0	0.76±0.07	0.09±0.04

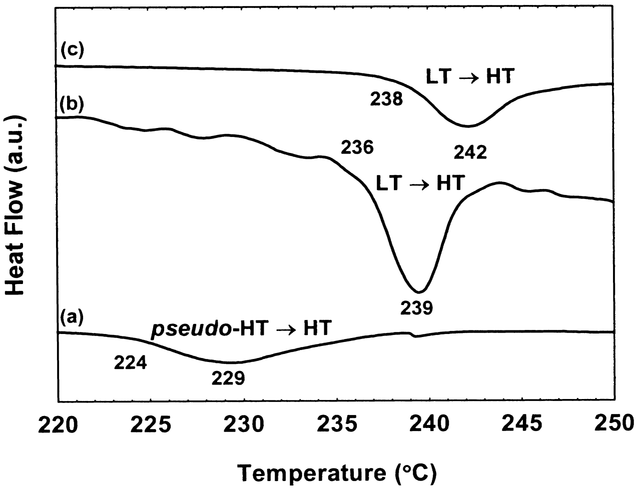

Fig. 2. DSC curves (a) after first hydrogenation, $Mg_{2-x}Al_xNiH_4$, (b) after cycling the hydride and (c) of LT2-Mg_2NiH_4 (without Al) as reference.

dynamically disordered HT phase, *pseudo*-HT→HT. In the latter, the disorder originates from the rapid reorientational motion of the [NiH_4]-complexes [15]. The phase transition remains reversible at the same temperature when repeating the DSC measurements 5–10 times between 200 and 280 °C. Further cycling causes the onset temperature to increase and to approach the conventional phase transition temperature (≈235 °C) where the monoclinic LT phase transforms to the cubic HT phase. X-ray diffraction analysis on the final product also confirms that the lattice at this time starts to revert to the LT structure. This is in accordance with the cycled $Mg_{2-x}Al_xNiH_4$ sample (Fig. 2b) for which the conventional LT→HT transition is observed with an onset temperature of 236 °C. This corresponds well also with the reference material (Fig. 2c) with onset temperature of 238 °C. The amplitude of the peak corresponding to the *pseudo*-HT→HT transition is smaller and wider than the conventional LT→HT transition peak as shown in Fig. 2b,c but is large enough to indicate that there is a significant difference between the *pseudo*-HT and the HT structure. It is clear that the Al-substitution has a profound effect on the phase transition temperature, which is decreased by ≈10 °C compared to non Al-containing Mg_2NiH_4. However, this effect is temporary as the cycled $Mg_{2-x}Al_xNiH_4$ shows nearly the conventional transition temperature and behaves similarly to LT2 Mg_2NiH_4.

The endothermic desorption peak ($Mg_2NiH_4 \rightarrow Mg_2Ni + 2H_2$) is not shown in Fig. 2. Several DSC measurements were made on the same samples and although the phase transition temperature remained constant at all times, the desorption temperature could differ by 200 °C depending on sample history. Rönnebro et al. [16] have shown that surface oxidation of Mg_2NiH_4 poisons the hydride and delays the desorption upon heating. This makes it difficult to relate the onset temperature of desorption with the effects of Al-addition in this experiment.

4. Conclusions

Aluminium was successfully included in the Mg_2Ni lattice by ball milling. Although the solubility was observed to be limited to ≈1 at.%, the substitution had an effect on the structure, phase transition temperature as well as the color of the hydrided sample, $Mg_{2-x}Al_xNiH_4$. The results show that the hydride lattice is affected by doping, which was indicated previously by theoretical calculations. The effect on the hydride properties was not permanent, as hydriding/dehydriding cycling of the aluminium containing sample reduced the influence of the doping.

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