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Structural studies of disordered Mg_2NiH_4 formed by mechanical grinding

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Abstract

The low temperature phase of Mg_2NiH_4 was mechanically ground in argon atmosphere. The ordered monoclinic structure was destroyed to form the disordered cubic structure, previously only found above 510 K. With a Guinier-Hägg X-ray camera the cell parameter was determined to be $a=6.492(3)$ Å. By performing a Rietveld refinement on neutron diffraction data it was confirmed that the disordered structure is similar to the high temperature form of Mg_2NiH_4 (space group *Fm3m*).

Keywords: Disordered Mg_2NiH_4; Mechanical grinding; Structural study

1. Introduction

Lately, research on Mg_2Ni–H systems has increased because of their promising characteristics for use in electric vehicles, which are demanding a lower material cost and higher hydrogen storage capacity than in the conventional secondary nickel–metal hydride batteries of AB_5-type.

The α and β hydride phases of Mg_2Ni have been investigated by several laboratories with respect to hydriding–dehydriding, structural, electronic, thermal and kinetic properties. The hexagonal Mg_2Ni dissolves hydrogen with a small expansion of the unit cell to form the α-phase ($Mg_2NiH_{0.3}$). When forming the β-phase (Mg_2NiH_4) the structure changes drastically and the hydrogen content becomes as high as 3.6 wt.%. The structural studies of the hydrides have been reviewed elsewhere [1], but here will be given a short summary of the latest information about the β-phase to emphasize the special features of the structure.

Mg_2NiH_4 is different from the more usual interstitial hydrogen storage hydrides. Its structure consists of tetrahedral NiH_4-complexes in a framework of magnesium ions. Above about 510 K the complexes and the Mg ions form a cubic high temperature (HT) phase with an antifluorite structure type. Inelastic neutron-scattering measurements revealed a fast local motion of the hydrogen atoms in the HT-phase which was interpreted as a reorientational motion of the hydrogen atoms around the nickel atoms, thus indicating a dynamical disorder [2]. When the sample is cooled below the phase transition, the rapid motion is ‘‘frozen’’ and the orientation of the complexes becomes ordered concomitant with a slight monoclinic distortion of the cubic lattice. In addition to this a phenomenon of microtwinning is introduced in the lattice. It was previously suggested that two different LT phases existed, but it is now accepted that there is only one phase; with (LT2) and without (LT1) microtwinning [3]. When investigating the LT phase with transmission electron microscopy (TEM) [4], only the LT2 phase was stable in the electron beam, thus enabling pictures to be taken. Thus the stacking faults increase the stability of the hydride against decomposition. So, a hydride without microtwinning is more suitable for hydrogen storage.

Recently the hydriding properties of the Mg_2Ni–H system synthesised by mechanical grinding to obtain nanocrystalline materials has been investigated by several groups. Zaluski et al. (1995) [5] have shown that by using high-energy ball milling to produce nanocrystalline Mg_2Ni the hydrogen absorption characteristics are superior and the activation is much easier. Kohno et al. (1996) [6] also ground Mg_2Ni mechanically obtaining an amorphous-like alloy with a discharge capacity of 750 mAh/g Mg_2Ni. Orimo et al. (1996) [7] claim that the hydrogen content in the Mg_2Ni–H system mechanically ground under a hydrogen atmosphere reaches 1.6 wt.% ($Mg_2NiH_{1.8}$) without changing the crystal structure of the matrix Mg_2Ni phase.

We chose another approach that to our knowledge has not been reported in the literature; the LT-phase of Mg_2NiH_4 was ball milled in argon atmosphere instead of

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ball milling the Mg_2Ni alloy under hydrogen pressure as has been done before. We found that the ordered monoclinic structure is destroyed by the mechanical stress to form the disordered cubic structure. The cubic Mg_2NiH_4 structure has previously only been found above 510 K. Therefore it is of interest to report that the NiH_4-complexes can exist even at room temperature when the disorder has been caused by the ball milling. We used Guinier-Hägg X-ray and powder neutron diffraction to characterise the samples as reported below.

2. Experimental

2.1. Sample preparation and Guinier-Hägg X-ray diffraction

The Mg_2Ni alloy was activated by cycling at about 350°C, using hydrogen pressures between 1 and 50 bar. This was performed in a stainless steel reactor equipped with a thermocouple in contact with the sample, thus monitoring the reaction temperature. The synthesis of the LT phase was performed in a similar way as described elsewhere [4]. When hydriding below 510 K a grey LT1 phase is formed. When cooling the HT phase the lattice undergoes a distortion forming an orange LT2 phase with microtwinning. All handling of the samples was carried out under argon atmosphere in a glove-box.

The samples were analysed using a subtraction-geometry Guinier-Hägg focusing camera with strictly monochromatised $CuK\alpha_1$ radiation ($\lambda=1.5406$ Å). Transmission data files were obtained with a computer-controlled microdensitometer, and the 2θ-scale was corrected by using silicon ($a=5.4309$ Å at 25°C) as internal standard. The samples were identified by refining the unit cell dimensions for possible phases with the program PIRUM [8]. Both the LT samples contain a small amount of MgH_2 and also some MgO.

2.2. Mechanical grinding

The mechanical grinding of the low temperature phase of Mg_2NiH_4 was performed in a planetary ball mill (Fritsch Pulverisette 7) at ambient temperature. The start materials were placed in a steel vial of 45 cm^3 with 5 steel balls of 15 mm diameter. The samples were handled in the argon filled glove box and the vials were sealed before being taken out to the ball mill.

2.3. Collection of powder neutron diffraction data

We collected a powder neutron diffraction pattern at the reactor in Studsvik ($\lambda=1.47$ Å, 295 K) of a deuterated sample of Mg_2NiD_4 which was ball-milled during one hour at 750 rpm (rounds per minute), in order to evaluate if it is similar to the high temperature neutron diffraction pattern.

3. Guinier-Hägg X-ray diffraction analysis of the mechanically ground samples

When grinding at low speed (200 rpm) the change from the crystalline monoclinic LT structure into the disordered cubic structure, space group *Fm3m* (no. 225), can be followed in the X-ray diffraction patterns shown in Fig. 1. The X-ray diffraction pattern of the cubic structure was indexed with the cell parameter refinements program PIRUM [8]. The cell parameter was determined to be $a=6.492(3)$ Å. There is a peak at $2\theta=19.4°$ ($d=4.56$ Å) which disappears when continuing the grinding. It corresponds to the (110) peak of the LT phase and it is a forbidden reflex in the F-centred cubic phase. This (110) peak disappears when the LT structure completely changes into the disordered cubic structure. It is interesting to note that the NiH_4-complexes in the disordered cubic structure still exist after such a severe treatment, although in a more and more disordered form as the ball milling continues.

The stacking faults have been observed to be pressure-sensitive. When applying an isostatic pressure to the LT2 phase, the amount of stacking faults will be reduced, thus changing to LT1 [9]. It has also been observed by Hayakawa et al. [10] that when grinding the Mg–50%Ni hydride the same change from LT2 to LT1 occurs. It was observed here that it takes a longer time for the LT2 phase than the LT1 phase to become disordered by ball milling, thus the microtwinning also stabilises the hydride in this respect.

We added Ni and Cu additives (grinding speed 400 rpm), with the intention to make an amorphous sample for an electrochemical test. After 5 h grinding the LT structure has changed into the cubic structure. After 20 h the sample still contains the cubic phase, but the peaks were much broader. Due to the Ni additive also a small amount of $MgNi_2$ was formed. We can not report any capacity since the samples corrode immediately when coming in contact with the electrolyte (6 M KOH). We are continuing the ball milling experiments in order to make an amorphous sample analogous with Orimo et al. (1996) [7].

4. Neutron diffraction analysis

The neutron diffraction data of the ball milled sample of Mg_2NiD_4 was refined with the Rietveld method program FULLPROF [11]. The sample also contained the LT-phase and MgO, which were included in the refinements. The intensities for the face-centred cubic cell of Mg_2NiD_4 in the neutron diffraction pattern are in close agreement with the neutron data for the high temperature phase collected by Yvon et al. [12], but the reflexes in the ball milled

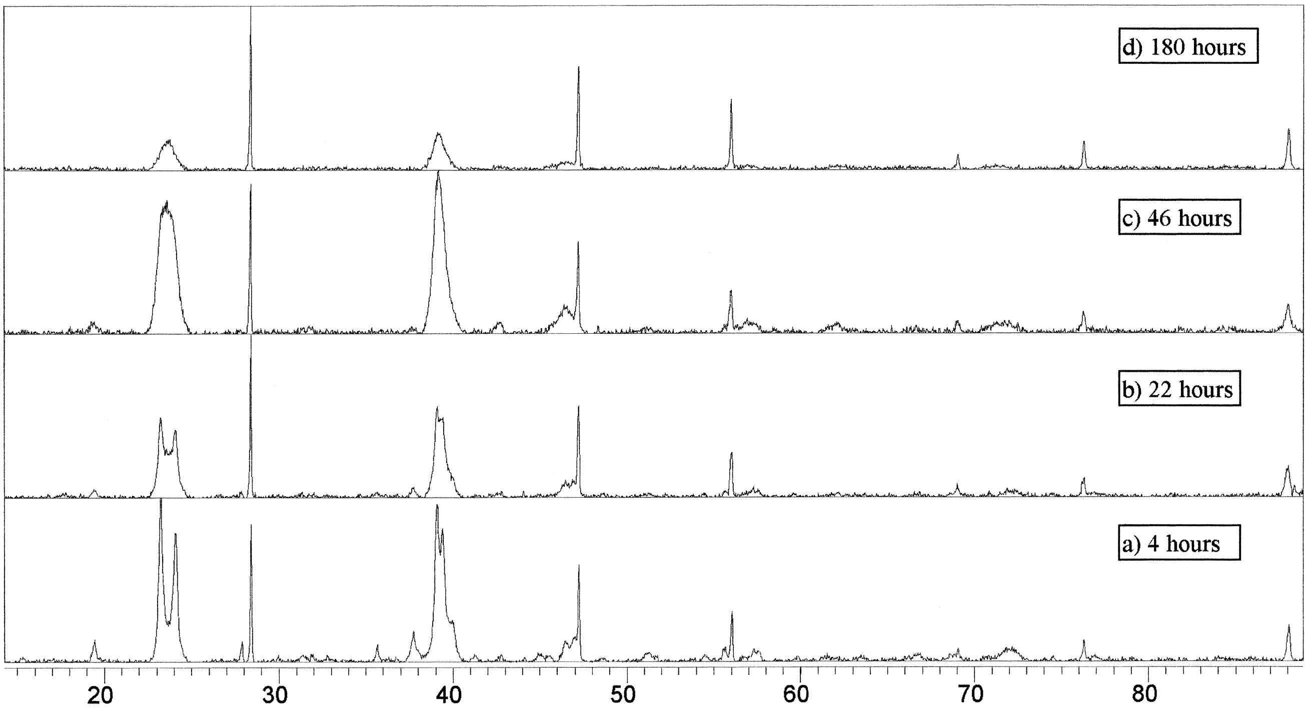

Fig. 1. The Guinier-Hägg X-ray diffraction patterns on a 2θ-scale for the LT-phase ground at 200 rpm; (a) 4 h, (b) 22 h, (c) 46 h and (d) 180 h.

sample are broader. The displacement factors were first refined as isotropic, B_0 ($\mathring{A}^2$), for both the metal and D atoms, but the graphical fit was not satisfactory. However, when refining the D atoms as anisotropic, β_{ij}, in accordance with Noréus et al. [2] the graphical fit became better and also decreasing the criteria of fit by about 4%. In space group *Fm3m* only one factor is needed to refine the β_{ij}'s since $\beta_{22} = \beta_{33}$ and the off-diagonal elements are zero in the 24*e* site [13]. Also the positional parameter for the D atom was refined. The scale factors, half width parameters (W) and cell dimensions were refined for the three phases. The positional parameters for the atoms in the LT-phase were also refined. In total 29 parameters were refined. Finally the criteria of fit for the disordered cubic phase converged to: $R_B = 3.70$, $R_F = 6.11$, and $R_W = 7.26\%$. The result from the refinement of the mechanically ground Mg_2NiD_4 presented in Table 1 is in agreement with the refinements made by Noréus et al. [2]. The higher displacement factors indicates a high degree of disorder, however. The observed and calculated diffraction patterns together with the difference plot from the Rietveld refinement are shown in Fig. 2.

5. Conclusions

High energy mechanical grinding changes the monoclinic LT structure into a disordered cubic structure where the metal atoms have an anti-fluorite (CaF_2) structure, space group *Fm3m* (no. 225). The diffraction patterns reveal a disordered structure with broad peaks which is expected since the sample has been under severe mechanical stress. The cubic form of Mg_2NiH_4 was previously observed only above 510 K when the high temperature allows the NiH_4-complexes to move around, thus this disorder has been interpreted to have a dynamical origin. When ball milling, mechanical stress disturbs the lattice to such a degree that it is observed by X-ray diffraction to be cubic and similar to the high temperature form. In this case the disorder could probably be described to have a static

Table 1
Atomic parameters from the Rietveld refinement for the ball milled Mg_2NiD_4 sample, space group *Fm3m*. The criteria of fit were $R_B = 3.70$, $R_F = 6.11$ and $R_W = 7.26\%$[a]

Atom	Site	*x*	*y*	*z*	B_0 ($\mathring{A}^2$)	β_{11} (Å)	$\beta_{22} = \beta_{33}$ (Å)	Occupance
Ni	*4a*	0	0	0	14(9)	–	–	1.0
Mg	*8c*	1/4	1/4	1/4	10(9)	–	–	1.0
D	*24e*	0.251(7)	0	0	–	0.02(2)	0.22(3)	0.67(1)

[a] The estimated standard deviations are given within parentheses.

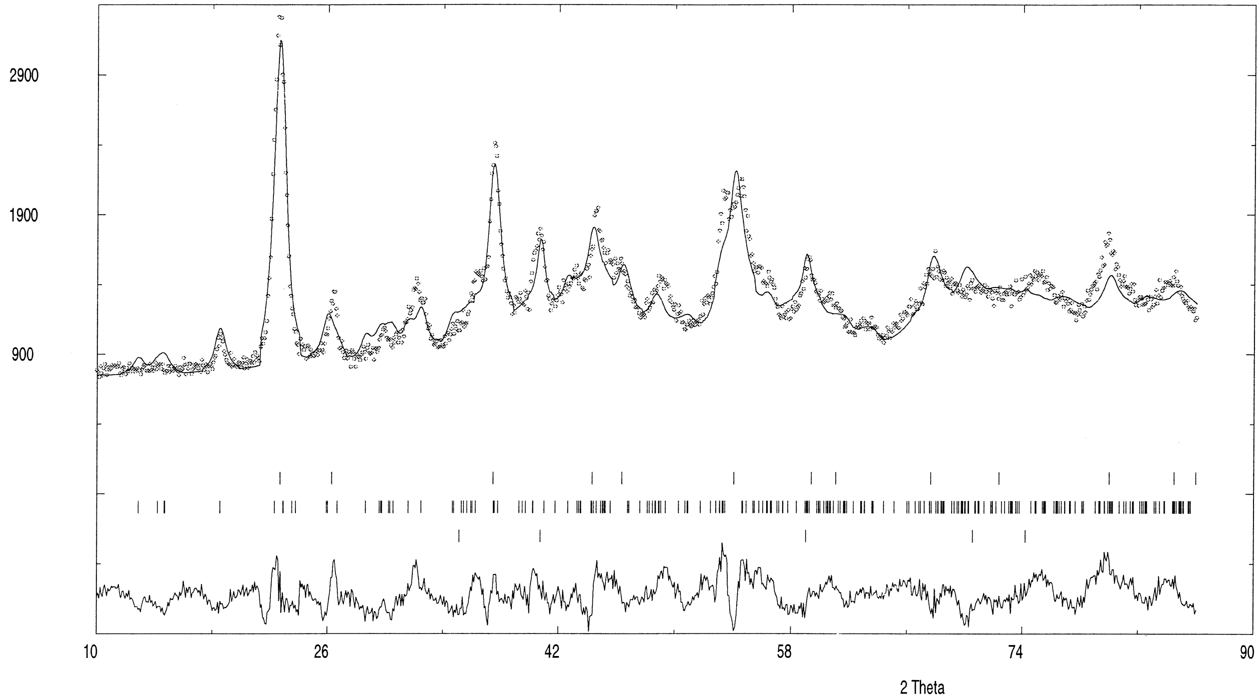

Fig. 2. The observed and calculated diffraction patterns together with the difference plot from the Rietveld refinement.

origin in order to clarify that it is not caused by a reorientational motion of the hydrogen atoms.

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