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Structural changes of Mg_2NiH_4 under high hydrogen pressures

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Abstract

In situ X-ray diffraction measurements were made on Mg_2NiH_4 under high pressures ($\leq$5 GPa) and temperatures ($\leq$600 °C), with and without an internal hydrogen source [$LiAlH_4$ or $NaBH_4$+$Ca(OH)_2$]. The transformation from the monoclinic low-temperatute (LT) form to a structure similar to the cubic high temperature form (pseudo-HT) was induced by application of pressure of 1.3~2.0 GPa. Upon heating to $\geq$200 °C under 5 GPa, a further transformation to the cubic HT form took place, followed by the appearance at $\geq$300 °C of a new high-pressure (HP) phase and in the presence of a hydrogen source a decomposition product NiH.

Keywords: Hydrogen storage material; Phase transformation; High pressure; X-ray diffraction

1. Introduction

Among all high-capacity hydrogen-storage materials, the most promising so far is the Mg–Ni–H system, the β-phase of which (Mg_2NiH_4) has a hydrogen content of 3.6 wt%. The structure of Mg_2NiH_4 consists of tetrahedral NiH_4-complexes in a framework of magnesium ions [1–4]. The hydride exhibits a transition at 235 °C. In the low-temperature (LT) phase, magnesium ions and NiH_4-complexes assume an ordered arrangement to form a monoclinic structure [5], whereas in the high-temperature (HT) phase, the arrangement becomes disordered to form a cubic antifluorite structure [6]. This phase transformation is, however, known to be severely disturbed by the internal stress. The HT phase was produced by ball-milling at room temperature [7] and also by static compression to 50 MPa during heat treatments [8]. The reverse transition from HT to LT phase was also affected by introduction of microtwinning, which is characterized by the appearance of a diffraction peak of a lattice spacing of 3.24 Å [5].

At high pressures, our previous experiments suggested the formation of a new high-pressure phase having a higher hydrogen content (>3.6 wt%) after recovery from heat treatments at 600 °C and 6 GPa [9]. This implied that a higher hydrogen electron complex could possibly be formed under these conditions [10]. The purpose of this paper is to report on in situ X-ray diffraction experiments on Mg_2NiH_4 at hydrogen pressures up to ~5 GPa and 600 °C, with an aim to clarifying the nature of high-pressure phase transitions.

2. Experimental methods

The Mg_2NiH_4 sample that contains about 20 wt% MgH_2 was supplied by JMC Japan. As an internal hydrogen source, a pellet of $LiAlH_4$ or a mixture of $NaBH_4$+$Ca(OH)_2$ was used. When heated, these materials decompose at ~300 °C and supply H_2 to the sample.

The experiments were performed at a synchrotron radiation source of Photon Factory (KEK) in Tsukuba, where a cubic-anvil press MAX80 is installed. This apparatus compresses a sample cell assembly (a cube of 8 mm in edge length) simultaneously from six perpendicular directions using a set of WC anvils. Details of the sample cell assembly were described elsewhere [11]. Briefly, a sample was a compressed pellet of ø1×(0.2~0.3) mm^3 in size, placed at the center of a pressure-transmitting medium (amorphous boron–epoxy resin composite), encased in a hydrogen-sealing capsule (NaCl) with a pressure marker (NaCl+BN) and the internal hydrogen source, and was surrounded by a graphite tube heater.

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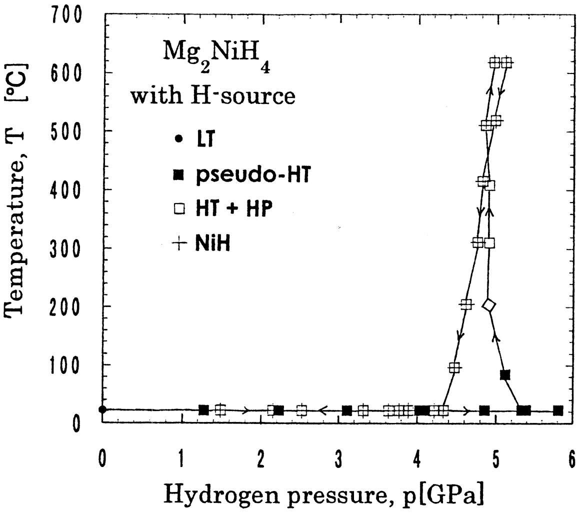

Fig. 1. Pressure–temperature history of the run with a hydrogen source $NaBH_4 + Ca(OH)_2$. Note that before the decomposition of the H-source (≤300 °C in the course of heating at 5 GPa), the pressure is simply a mechanical pressure instead of a hydrogen pressure. Observed phases are shown by symbols.

The X-ray diffraction (XRD) was measured by the energy-dispersive method, using an SSD placed at a fixed angle from the incident white X-ray beam. The incident X-rays were collimated to a beam of 0.2×0.1 mm^2, with which an overall accuracy in the lattice parameter of approximately 0.05% was attained in a measuring time of 60~300 s. The actual pressure in the sample cell was determined to be 0.03 GPa by measuring the lattice parameter of NaCl using a Decker scale [12].

Measurements were made in the following way. A sample was compressed to ~5 GPa at room temperature, heated subsequently to ~600 °C, followed by cooling to ambient conditions. Such runs were repeated three times; twice with a different hydrogen source each time and then without a hydrogen source for reference. The XRD was measured at appropriate intervals of pressure and temperature. Actual pressure–temperature histories of the two runs are shown in Figs. 1 and 2.

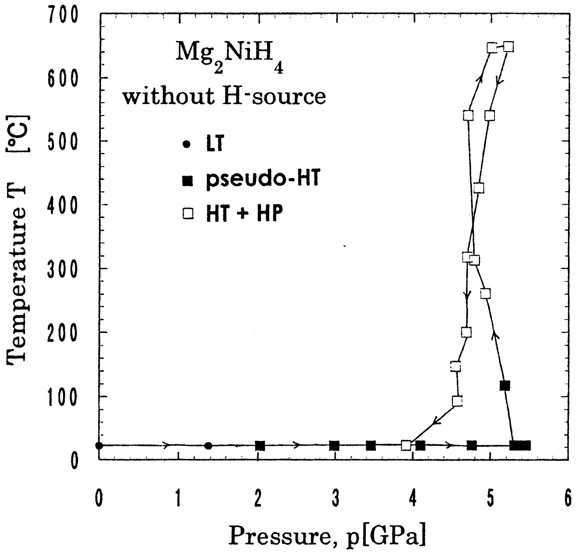

Fig. 2. Pressure–temperature history of the run without a hydrogen source. Observed phases are shown by symbols.

To identify diffraction peaks in the observed spectra, a semi-exhaustive trial-and-error program TREOR [13] was adopted. The lattice parameters were determined by PIRUM [14], a Fortran program for least-square refinement.

3. Discussion of in situ XRD spectra

Before starting compression and heating of the sample, an XRD spectrum was taken under ambient conditions, as shown in Fig. 3a. The relative peak intensities indicate that the starting material consisted of the LT-phase of Mg_2NiH_4 with some amount of microtwinning and ca. 20% MgH_2. The MgH_2 was found to exist in all the following measurements. In the process of compression at room temperature, a transformation of the LT-form into a cubic form similar to the HT-structure started between 1.3~2.0 GPa. This structure is similar to the one observed in ball-milled Mg_2NiH_4, and is here called pseudo-HT structure. Fig. 3b shows this pseudo-HT phase coexisting with a remaining LT phase. Both these phases exhibit broad diffraction lines, reflecting their sensitivity to internal stress. Under 5 GPa, a transition to the cubic HT structure occurred at ≥200 °C. On further heating, a set of strong diffraction peaks appeared at ≥300 °C and grew in intensity together with some small peaks, as shown in Fig. 3c and 3d. (These strong peaks are labelled by open triangles and designated by HP in the figures). Comparison of these figures with Fig. 3f, which was observed without a hydrogen source, reveals the following features: The set of HP diffraction lines as well as those of MgO appeared both with and without a hydrogen source. In contrast, NiH peak(s) appeared only in the presence of a hydrogen source. MgO is probably the product of reaction with moisture in the cell, whereas NiH should be the result of disproportionation reaction

$$2Mg_2NiH_4 + H_2 \rightarrow 4MgH_2 + NiH$$

The HP lines may possibly be due to the occurrence of a new high pressure (HP) phase, whose strong intensities suggest Ni as a major constituent of the phase. Throughout these measurements, results obtained with two different hydrogen sources were the same, which excludes the possibility of decomposition products of the hydrogen sources contaminating the sample.

After quenching to room temperature, all the phases were retained as shown in Fig. 3e. After subsequent decompression, the pseudo-HT phase remained with a

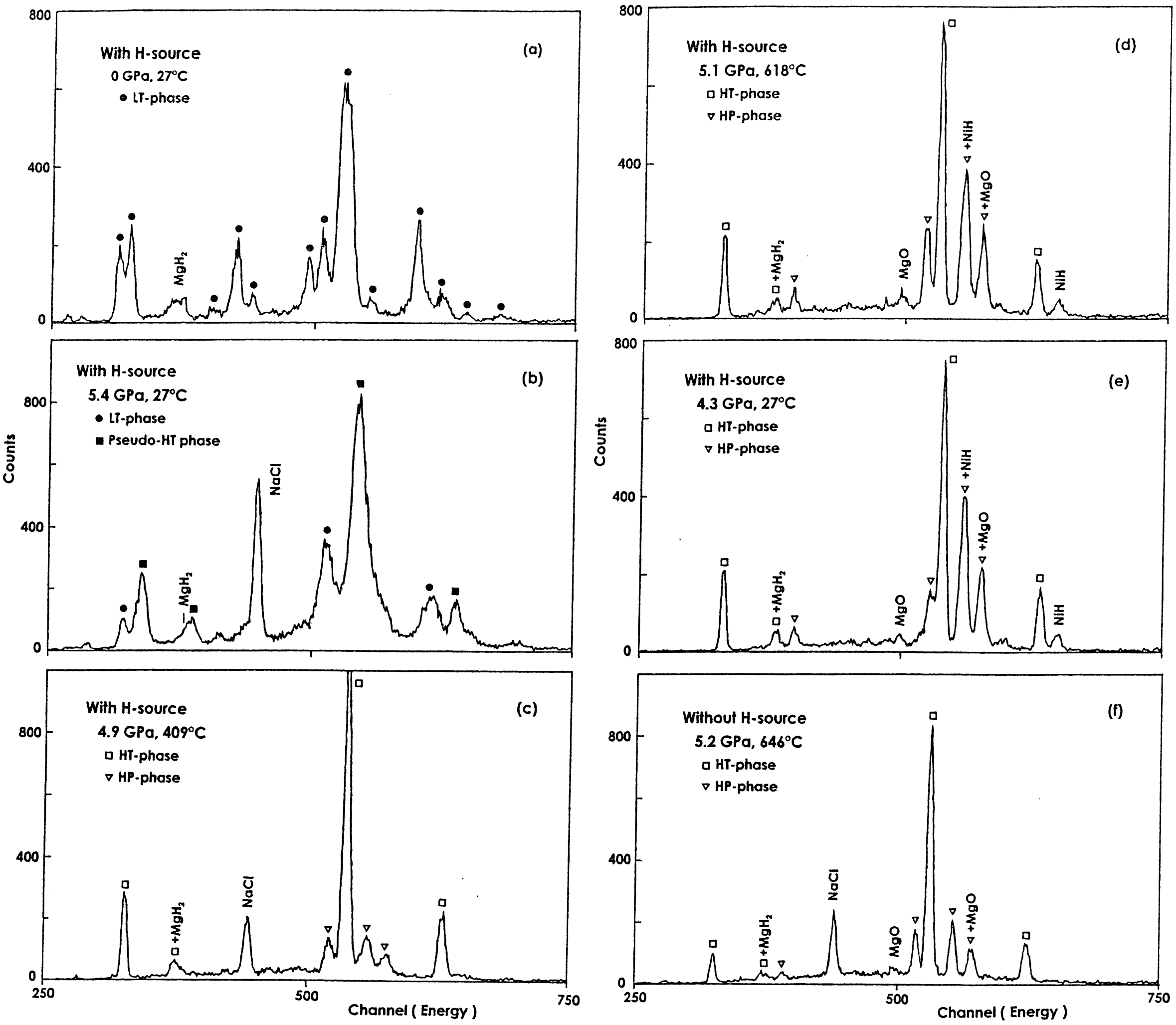

Fig. 3. XRD spectra observed in the run with a hydrogen source (a)–(e), and those without a hydrogen source (f). For a hydrogen source, a mixture of $NaBH_4 + Ca(OH)_2$ was adopted.

lattice parameter $a = 6.54$ Å [7,15], which is close to the value previously obtained by ball-milling. As the quenched samples consisted of a mixture of several different materials and different phases, their characterization has not been very successful so far.

With our previous high-pressure experiments, the present results do not appear to be entirely consistent. There, a larger amount of the LT-phase remained with a less deformed structure than in the present case. The present in situ experiment does not provide evidence in support of the formation of a Mg_2Ni-hydride with higher hydrogen contents and thus the formation of a 20-electron complex in this compound at high hydrogen pressures [10]. Although the structure of a new HP phase has not been determined so far, its appearance irrespective of hydrogen pressures precludes the possibility of its being a higher-hydrogen compound based on Mg_2Ni.

For a possible origin of the HP phase, we suggest the following. The above disproportionation reaction proceeds in two-steps;

$$Mg_2NiH_4 \rightarrow MgNiH_2 + MgH_2, \tag{1}$$

which yields $MgNiH_2$ as a HP phase, and then its reaction with hydrogen

$$2MgNiH_2 + H_2 \rightarrow 2MgH_2 + NiH \tag{2}$$

In fact, it was suggested in our previous paper [9] that $MgNiH_2$ thus formed at high hydrogen pressures becomes amorphous after quenching and acquires a higher hydrogen capacity (a-$Mg_{1.02}NiH_{2.6}$).

More detailed structure analysis of HT and HP phases will be reported in our forthcoming paper.

4. Conclusion

The structural changes of a sample of the LT-form of Mg_2NiH_4 were investigated by in situ XRD up to 5 GPa and 600 °C. By compression at room temperature, the symmetry increased at 1.3~2.0 GPa to form a nearly cubic structure similar to ball-milled Mg_2NiH_4 (pseudo-HT). At 5 GPa, the pseudo-HT phase transformed above ~200 °C to a cubic HT structure, followed by the appearance at ~300 °C of a new phase (HP) plus a small amount of MgO, and in the presence of a hydrogen source a small amount of NiH as well. A possible mechanism of formation of these high-pressure, high-temperature products is suggested.

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