

HIGH-PRESSURE PHASES IN THE MAGNESIUM – TRANSITION METAL – HYDROGEN SYSTEMS

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Introduction

It has been found recently that the high-temperature treatment of powder mixtures of magnesium and transition metal dihydrides (TM = Ti, Zr, V or Nb) under high hydrogen pressure results in formation of new compounds in the ternary magnesium – transition metal – hydrogen systems [1-3]. The interest in the new intermetallic hydrides increased due to partial reversibility of dehydrogenation of the new high-pressure phases: the $Mg_9Zr_2H_x$ phase has been reported to release and reversibly absorb 3 to 3.5 wt.% H_2 without decomposition or the change of the crystal structure at temperatures 250 to 320°C [4]. Recent *ab initio* calculations of the chemical bonding in the Mg_7TMH_x compounds were brought to modeling of the inelastic neutron scattering spectra of Mg_7TiH_x [5] and anticipated the experimental study. The experimental study of the properties of the new compounds is, however, complicated because synthesized samples include admixtures of the initial binary hydrides. Our work is aimed at preparation of the single-phase samples of the new intermetallic hydrides.

Experimental

In this work we used commercial Mg dihydride of the composition $H/Mg=1.9$ and Ti and Zr dihydrides. All operations with MgH_2 were carried out in the dry nitrogen glove box. Ti and Zr dihydrides with compositions $H/TM>1.9$ were produced at low hydrogen pressures using a Sieverts-type apparatus and ground in air to a particle size of less than 10 μm . The experimental stock was prepared by mechanical mixing of the dihydrides in the molecular ratio $MgH_2 : TMH_2 = 7 : 1$. Finally, the powder mixtures were ground in mortar until homogeneity in color.

The thermobaric treatment was carried out either in hydrogen atmosphere or in inert medium. The procedure usually included primary loading to 1.5–2.5 GPa and temporary heating to 300–600°C at this pressure. In some experiments, hydrogen atmosphere was generated at this stage by means of chemical decomposition of metastable AlH_3 .

Pressure was increased then to the final value at temperatures of 250°C or below, and final thermal treatment of the sample was carried out at a temperature in the range of 400–800°C. After 1–5 h maintenance the sample at the final T and P values, the high-pressure cell was cooled and decompressed. The treated samples were recovered from the cell in the glove box.

The first series of the high-pressure experiments demonstrated that the MgH_2 – TMH_2 mixtures are chemically very active at high pressures and react with metals that are immiscible with magnesium at atmospheric pressure, e.g., with molybdenum. The main part of our experiments was carried out therefore with the use of the NaCl ampoules.

The X-ray diffraction was measured in air or under the vaseline layer using diffractometer *Siemens D500* with the $CuK_{\alpha 1}$ irradiation.

Results and discussion

For the $7MgH_2+ZrH_2$ mixture, we tested first whether the hydrogen atmosphere is a necessary condition for synthesis of the intermetallic hydride. For this purpose, two treatment experiments were made with the final values of $P=5$ GPa и $T=600^\circ C$ and the 3-hour exposition time at the final parameters. One experimental sample was treated in the hydrogen environment, and the other sample was treated in inert medium. The X-ray diffraction patterns of the two samples are much the same, they are represented by the top curves in Fig. 1. The curves include the peaks of the initial β - MgH_2 phase, the high-pressure γ - MgH_2 phase, the MgO and $NaCl$ impurities, but there are no ZrH_2 peaks. Instead, new peaks are observed in the pattern due to the high-pressure phase formed during treatment.

A more complete reaction of the initial hydrides was observed for the samples that were heated to 600°C for a short time at the primary stage of loading. The bottom pattern in Fig. 1 does not include peaks corresponding to ZrH_2 as well to both MgH_2 phases. The positions and the relative intensities of the low-angle peaks in the pattern

resemble those shown in the diffraction pattern of the $\text{Mg}_2\text{Zr}_3\text{H}_x$ phase with the $C2/m$ monoclinic structure of the metal sublattice [6]. The same monoclinic structure was also reported for the metal sublattices of MgNb_2H_x [3] and for MgZr_2H_x later [7].

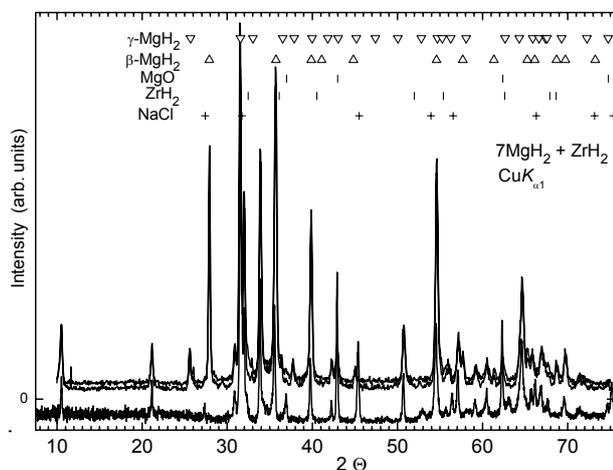


Fig. 1. X-ray diffraction patterns of the $7\text{MgH}_2+\text{ZrH}_2$ powder mixtures treated at high pressures and temperatures. *Top curve*: the sample was treated in inert medium with the final values of $P = 5$ GPa and $T = 600^\circ\text{C}$ during 3 h. *Middle curve*: the same treatment, but in the hydrogen environment. *Bottom curve*: the sample was treated in inert medium with the short-term heating to $T = 600^\circ\text{C}$ at the primary stage of loading and the final pressure value $P = 7$ GPa. *Bar diagrams* show the peak positions of $\gamma\text{-MgH}_2$, $\beta\text{-MgH}_2$, ZrH_2 , MgO and NaCl .

We attempted to fit the bottom pattern in Fig. 1 using the multi-phase Rietveld analysis program, DBWS-9411. We find that the peak positions are well reproduced within the monoclinic structure with the lattice parameters $a=5.818 \text{ \AA}$, $b=3.368 \text{ \AA}$, $c=8.61 \text{ \AA}$ и $\beta=103.0^\circ$. But the intensity fit is not a success so far. This fact leaves some uncertainty whether the sample obtained is single-phase.

The $\text{MgH}_2\text{-TiH}_2$ system is less studied here. The maximum treatment parameters for the $7\text{MgH}_2+\text{TiH}_2$ mixture were $P=9$ GPa and

$T=800^\circ\text{C}$. The X-ray pattern of thus treated sample includes the diffraction peaks of the superstructured Mg_7TiH_x phase, reported in Ref. [1]. However, the reaction was not complete due to insufficient duration of the thermobaric treatment (15 min) in this experiment, and the initial dihydrides were also represented in the diffraction pattern. Both the positions and the intensities of diffraction peaks are well described within the known structures.

Conclusions

New hydrides in the ternary magnesium – transition metal – hydrogen systems have their stability regions under high pressure. These high-pressure phases are formed in the $\text{MgH}_2\text{-TMH}_2$ mechanical mixtures under $P\text{-}T$ conditions within their stability regions due to sintering provided that the diffusion of the components is ensured. In the Mg-Zr-H system, the monoclinic phase is observed in a rather wide range of the Mg/Zr ratio.

References

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