Hydrogen Distribution in Partly Desorbed MgH₂ Samples

LUSHNIKOV Stepan Alexandrovich¹,a*, FILIPPOVA Tatyana Victorovna¹,b, BOBRIKOV Ivan Anatolievich²,c.

¹Department of Chemistry Lomonosov Moscow State University, Leninsky Hills 1/3, 119991 Moscow, Russia
²Joint Institute for Nuclear Research, ul. Jolio-Couri 6, 141980 Dubna, Moscow region, Russia
alushnikov@hydride.chem.msu.ru, btania.filippova@inorg.chem.msu.ru, civan-dubna@ya.ru

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Abstract. The structure of MgH₂ samples has been investigated by the neutron diffraction method at room temperature and 5 K. Samples of MgH₂ have been prepared with vacuum extraction technique at high temperature. Obtained neutron data demonstrated that samples contain coexisting Mg and MgH₂ phases in different rate. The distribution of hydrogen atoms in the structure of the samples is comparable at both temperatures. Collected neutron data and results of X-ray analysis show that microstructure of the samples is different at room and at low temperature. Non-stability of partly desorbed MgH₂ samples after low temperature treatment has been discussed on basis of different diffusion of hydrogen atoms in varied microstructure.

Introduction

Hydrogen is a promising energy source for the near future instead of fossil fuels. In order for hydrogen become more appropriate for practical applications, it must be stored safely and compactly. Hydrides of metals and intermetallic compounds are potential hydrogen storage materials. Magnesium hydride (MgH₂) contains about 7.6 mass percent of hydrogen. Also this material is cheap, abundant and friendly for environment. But the high temperature of decomposition (about 300°C) and slow kinetic of reaction with hydrogen restrain magnesium hydride for practical application. At present time in many works were presented recent results in relation how to modify these properties of MgH₂ [1, 2]. With catalytic additives and nanostructuring of the magnesium were improved kinetic and stability of MgH₂ [3, 4]. The study of the MgH₂ structure allows determining of the positions of hydrogen atoms in crystal lattice. In literature was described that magnesium hydride in ambient conditions has a tetragonal structure (α-MgH₂ modification, P4_2/mnm, No. 136) with hydrogen atoms distributed in Mg₃₃ triangles [5]. The bonds between magnesium and hydrogen in α-MgH₂ are ionic with substantial covalent quantity [2]. Under high pressure, the α-MgH₂ modification was transformed into γ-MgH₂ with an orthorhombic structure (Pbcn, No. 60), which is metastable in ambient conditions [6]. And recently in review [2] was described β-MgH₂ form with modified CaF₂ structure (Pa-3, No. 205). In present work we have analysed the structure of partly desorbed MgH₂ samples at room temperatures and 5 K by neutron diffraction method. This method allows determining hydrogen atoms on the interstitial sites of the metal matrix of hydrides. The different temperature of the experiment (room and 5K) leads to the redistribution of hydrogen atoms in the positions of the structure. Therefore we think to monitor a hydrogen atoms migration between different sites of the crystal lattice.

Methods

Samples of magnesium hydride were prepared from the powder of MgH₂ using vacuum extraction technique (thermodesorption) at the high temperature (about 300°C). All the samples were analyzed by powder X-ray diffraction using a Rigaku D/max-2500 diffractometer (Cu Kα₁ radiation). The neutron diffraction experiments were performed at room temperature and 5 K at the High-Resolution Fourier Diffractometer (HRFD) at the IBR-2 pulsed reactor in the Join Institute of Nuclear Research in Dubna town of Moscow region. Samples of MgH₂ with hydrogen have strong
incoherent absorption of neutron. Therefore for neutron experiment usually are prepared samples with deuterium. Deuterium substitution markedly reduces incoherent neutron scattering, substantially improving the quality of neutron diffraction patterns. But in our case we were able to achieve quality neutron data for all samples with hydrogen. Obtained neutron and X-ray data were refined by the Rietveld method.

Results

X-ray analyses showed that partly outgazed samples of MgH\(_2\) contain Mg and MgH\(_2\) phases with different ratios. Cell parameters of these phases are comparable with the lattice parameters in references [5, 7]. It was established that samples with ratio of phases Mg > MgH\(_2\) after fast quenching at low temperature (77 K) become unstable. In ambient conditions all these samples decomposed soon into magnesium. Neutron diffraction experiment was performed with the samples, which have phase ratio corresponding to 75% of Mg and 25% of MgH\(_2\). Obtained experimental neutron diffraction spectra demonstrated that samples contain some small impurities, corresponding to the MgO phase. Additionally, neutron diffraction data showed that the phase ratio of the studied samples (75% of Mg and 25% of MgH\(_2\)) was close to the ratio, obtained from the X-ray analyses. Due to more deep penetration of neutron beam in comparison with X-ray, this indicates, that both Mg and MgH\(_2\) phases are equally distributed in material of the sample powder.

The neutron structure data at low (5K) temperature showed that hydrogen was distributed in the sites of MgH\(_2\) phase of sample (Fig. 1, Table 1). The Mg phase has the site positions without of hydrogen. Analyses of the neutron data at room temperature demonstrated that distribution of hydrogen in the structure was the same as at low temperature (Fig. 2, Table 1). At room temperature, hydrogen atoms also occupied position only in the sites of MgH\(_2\) phase, while the sites of Mg phase weren’t occupied. As a result, neutron experimental data showed that at room and low temperature hydrogen in the structure was in ordered condition.

As was revealed primary, similar hydrogen distribution was monitored in the partly desorbed samples of MgH\(_2\), which were quenched at low temperature. Neutron data showed that in these samples hydrogen occupied sites in the matrix of MgH\(_2\) phase. The sites in the lattice of Mg were vacant of the hydrogen atoms. Neutron diffraction results of the non-quenched partly desorbed samples of MgH\(_2\) demonstrate that hydrogen was distributed analogously. The hydrogen atoms are located on the interstitial sites of the lattice of MgH\(_2\) phases, whereas the lattice of Mg phase contains no hydrogen atoms. Consequently, in both types of the samples hydrogen atoms are located in the \(\beta\)-hydride phase of MgH\(_2\). In the lattice of \(\alpha\)-MgH\(_2\) hydride and \(\alpha\)-phase of Mg the hydrogen atoms were not detected. This means that hydrogen atoms relocation between \(\alpha\)-MgH\(_2\) hydride and \(\alpha\)-phase of Mg was not observed for the both quenched and non-quenched samples.
In most cases hydrides at low temperature have ordered hydrogen atoms in the structure. Decreasing of the temperature leads to redistribution of hydrogen atoms in the sites of structure. In our case at room temperature occurs formation of saturated MgH$_2$ with ordered hydrogen in the structure. Decreasing of temperature didn’t change this ordered condition of hydrogen atoms. Analyses of obtained neutron spectra showed that samples under low and room temperature have a different morphology of metal matrix. The sample at low temperature was crystallised better than once at room temperature. It’s known that heat treatment at high or low temperature has a significant influence on the size of grains in the polycrystalline body of the material. As a rule, fast quenching of samples from steel material at low temperature leads to decreasing of the grain size and changing of microstructure of this material. In reference [8] is known, that hydrogen plays the
role of the defects in metal matrix of $d$-metals hydrides. The presence of hydrogen atoms inside of the crystal lattice of $d$-metals hydrides leads to appearing in the metal matrix different polymorph transformations. As a consequence, under this process the microstructure of material and size of grain also have been changed. These polymorph transformations of the metallic lattice occur in analogy with the crystal structure transformations under high pressure. Therefore, we can think that quenched at low temperature samples of MgH$_2$ also have modified microstructure of the metal matrix. Consequently, diffusion of hydrogen atoms and kinetic of reaction with hydrogen of the studied MgH$_2$ samples have been changed. We can suggest that varied microstructure of the MgH$_2$ samples leads to decreasing their stability.

Table 1. The neutron diffraction data of the MgH$_2$ samples.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Position type</th>
<th>Occupancy</th>
<th>Atomic coordinates</th>
<th>Phase composition</th>
</tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>0.333 0.667 0.25</td>
<td>Mg 75%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>0.333 0.667 0.75</td>
<td>Mg$_2$H$_2$ 25%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>0.305(2) 0.305(3) 0</td>
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</tr>
<tr>
<td>Mg</td>
<td>2c</td>
<td>0.9</td>
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<td>Mg 75%</td>
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<tr>
<td>H</td>
<td>2d</td>
<td>0</td>
<td>0.333 0.667 0.75</td>
<td>Mg$_2$H$_2$ 25%</td>
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<tr>
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<tr>
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<td>0.305(3) 0.305(2) 0</td>
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</tbody>
</table>

Summary

The structure of the partly desorbed samples of MgH$_2$ has been investigated by neutron diffraction method at room temperature and 5 K. The neutron data showed that at both temperatures hydrogen was distributed in the sites of the MgH$_2$ phase, while the sites of Mg phase weren’t occupied with hydrogen. It was found that morphology of the material of MgH$_2$ samples at room and 5 K temperature was different.

Reference


