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Magnesium hydrides and their phase transitions

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ABSTRACT

The mechanism of phase transitions in magnesium dihydrides is explored with the aim how to find the ways for lowering crystal structure stability and facilitate hydrogen desorption. After recapitulation of transition metal hydrides properties, a possible mechanism of fluorite-rutile type displacive phase transition is proposed.

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Introduction

Magnesium hydride is studied as a material with large hydrogen storage ability, its hydrogen mass absorption capacity is 7.6 wt. %. However, major drawbacks as slow absorption kinetics or elevated decomposition temperature [1] impede its utilization. Such undesirable behaviour is a consequence of strong Mg–H bonds in magnesium hydrides.

Our considerations will be limited to magnesium dihydrides, different structures reported in literature will be summarized, but finally only the most stable rutile-type structure together with the fluorite-type structure widely observed in the hydrides of elements from the vicinity of magnesium in the periodic table will be considered in more details.

With the aim to find under which conditions the fluorite-type structure can be formed in the case when the rutile-type structure is more stable, the transition metal hydrides from the beginning of 3d series will be discussed. Possible displacive nature of the fluorite-rutile type phase transition is then described indicating a qualitative similarity with the

martensitic transformations in steels. Such transformations are treated in detail in the book written by Prof. Christian [2].

This short paper poses a question whether it could be feasible to improve applicability of magnesium hydrides for hydrogen storage by formation of less stable crystal structures. It will be shown that the fluorite-type structure of magnesium hydride as a non-equilibrium state has different bonding properties in comparison with the same structural state of transition metal hydrides where this structure-type is the most stable structural state. At high hydrogen concentrations, the hydrogen atoms occupy the lattice interstitial sites by pairs in the former case while they are present as individual separate atoms in the latter case.

Structures of magnesium hydrides

Three different crystal structures were reported for magnesium dihydrides in Ref. [3] and are listed in Table 1: α -MgH₂ with rutile-type tetragonal structure at ambient conditions,

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Table 1 – Three crystal structures of MgH₂. The lattice parameters *a*, *b*, *c* [3] are expressed in nm and the volume-per-formula *v* in nm³.

	<i>a</i>	<i>b</i>	<i>c</i>	<i>v</i>
α-MgH ₂	0.4517	0.4517	0.3020	0.03081.
β-MgH ₂	0.483	0.483	0.483	0.02817
γ-MgH ₂	0.453	0.544	0.493	0.03037

β-MgH₂ with fluorite-type structure and γ-MgH₂ with orthorhombic structure, both latter structures arising at high pressure. While for the high-pressure phase β-MgH₂, the volume-per-formula is about 8.6% lower with respect to the reference α-MgH₂ phase at ambient conditions, the volume-per-formula is only about 1.4% lower for the γ-MgH₂ phase. According to [4], the α-MgH₂ and γ-MgH₂ phases coexist between the pressures of 0 and 9 GPa. Other more complex phases that were reported only under particular conditions, including cotunnite structure [4], can appear at higher pressures. According to [5], the β-MgH₂ phase appeared during compression at the pressure that lowered the volume-per-formula down by about 21% of the reference volume, but the β-MgH₂ phase persisted during decompression to the volume-per-formula that was 8.4% lower than the reference one. The number of magnesium nearest-neighbour hydrogen atoms in α-MgH₂ and in γ-MgH₂ is six in both structures what is directly related to only small differences among the volumes-per-formula. On the other hand, the number of magnesium nearest-neighbour hydrogen atoms in β-MgH₂ is eight indicating that the phase transition α → β is associated with a qualitative change of the magnesium-hydrogen bonding revealed by the magnesium atom coordination.

Transition metals hydrides

A short-range attractive interaction between hydrogen interstitial atoms was found in the nickel matrix [6]. Due to such interaction, the hydrogen concentration grows in the tensile strained regions. First, the octahedral interstitial sites are occupied and when the hydrogen atoms start to inhabit the tetrahedral interstitial sites, the hydrogen concentration can even further increase. However, besides the hydrogen–hydrogen (H–H) separation, the hydrogen-metal (H–M) spacing is crucial for hydride properties. The distance between the hydrogen atom in an interstitial position and the neighbouring metallic atoms varies with the interstitial site type. Assuming a hydride with the fluorite-type structure, with the lattice parameter *a_f*, the H–M distances are *a_f*/2 for the octahedral interstitial position and *a_f*√3/4 (about 0.433 *a_f*) for the tetrahedral interstitial position. The metallic atoms are in the fluorite-type structure in the atomic sites of the FCC lattice and the hydrogen atoms occupy the tetrahedral interstitial sites giving thus the MH₂ stoichiometry. When the hydrogen atom is put at the centre of the triangular metallic faces parallel to the {111} plane, the H–M distances further decrease to *a_f*/√6 (about 0.408 *a_f*). The number of the metallic nearest-neighbours decreases from 6 for the octahedral interstitial position, via 4 for the tetrahedral interstitial position, down to

3 for the planar triangular face. In fact, the latter case corresponds to the rutile-type hydride structure. The tetragonal rutile-type lattice parameters are *a_r* and *c_r*. For the constant formula-cell-volume of the MH₂ metallic dihydride, the basis

parameter *a_r* is equal to $a_f \left(\frac{3}{4}\right)^{1/3}$ (about 0.909 *a_f*) assuming that the *c_r*/*a_r* ratio is equal to 2/3, what is almost the case for αMgH₂, *c_r*/*a_r* = 0.6686. The H–M distances are then (11/18√2) *a_r* (about 0.432 *a_r*), i.e. about 0.393 *a_f*, that is even lower than *a_f*/√6 (about 0.408 *a_f*). Therefore, considering the transition between rutile-fluorite type structures and assuming the preservation of the formula-cell-volume, the H–M distances is increased by about 10% for the planar-tetrahedral hydrogen coordination (from about 0.393 *a_f* to 0.433 *a_f*).

It is reported in Ref. [7] that the energy of binary hydrides is composed of three terms: the structural transformation energy, when the crystal structure of the host metal is different from the hydride, the lattice expansion energy, due to increasing hydrogen content, and the hydrogen insertion energy (*E_{ins}*). The last term is a function of hydrogen-metal interatomic distance. Contrary to the transformation and lattice expansion energies that represent positive contributions to the hydride formation energy, the insertion energy has the negative sign. When the hydrogen-metal H–M interatomic distances decrease, the insertion energy is growing and the H–M bonds are becoming less strong. For several transition metal hydrides, the hydrogen insertion energy *E_{ins}* (expressed in kJ/molH₂) was proposed in Ref. [7] to be interpolated by the following formula: 13930(10R)^{-7.723}–268, where R is the H–M distance expressed in nm. The values for the selected transition metals and magnesium hydrides are marked in Fig. 1.

Various data for the hydrides of the transition metals from the beginning of the 3d series together with magnesium are summarized in Table 2. The lattice parameters of hydrides are

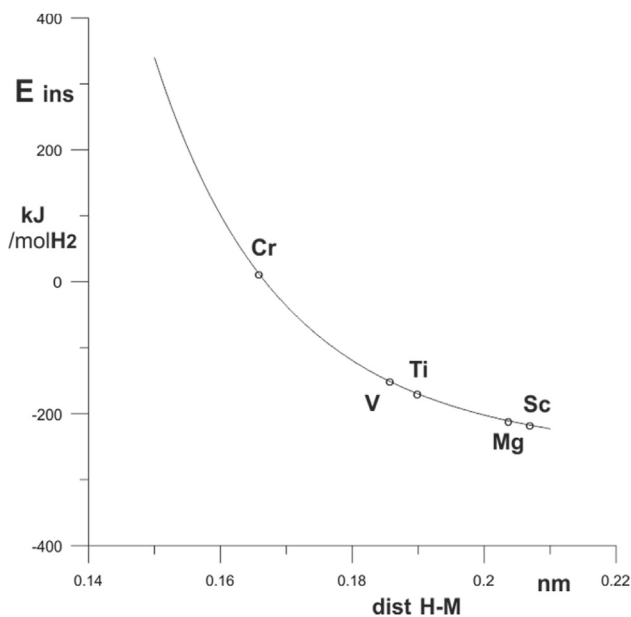


Fig. 1 – Hydrogen insertion energy as a function of the distance between the hydrogen-metal (H–M) nearest-neighbour atoms according to [7].

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