Selected Metal-Hydrogen Systems under High Hydrogen Pressure

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Development of high hydrogen pressure technique and its application for syntheses of hydrides of transition metals (with focus on MnH_x and hydrides of Ni-based alloys) and hydrides of Laves phase alloys have been briefly reviewed. Experimental prove of the existence of ferromagnetic *fcc* Mn is given and a unique role of Mn in transformation of RMn_2 Laves phase alloys into non-interstitial RMn_2H_6 (R = Y, Er, Dy, Ho, Gd) hydrides is presented.

Key words: Transition metals, Laves phase alloys, Hydrides, High pressure

1. INTRODUCTION

The "father of high pressure research" P.W. Bridgman, whose pioneer works were awarded with a Nobel Prize in 1946 has invented and constructed a number of high pressure equipments which then he employed in his outstanding studies of properties of matter at extremely high pressure conditions [1]. His excellent equipments were still not good enough to check the prediction of Wigner and Huntington [2] about transformation of molecular hydrogen into the metallic state at 30 GPa. It could be expected that this "metallic hydrogen dream" together with experimental high pressure tools created already by Bridgman will stimulate research on hydrogen and hydrogen-metal systems at very high pressure conditions. However, for quite a long time researchers feared to undertake such studies because of well known "hydrogen embrittlement" responsible for dangerous damage (sometimes explosions) of iron base vessels being in contact with hydrogen at high pressure. An essential breakthrough took place in 1966 in the Institute of Physical Chemistry of the Polish Academy of Sciences (IPCh PAS) where the first synthesis of NiH directly from elements has been done by Baranowski and Wiśniewski [3] at 25 ℃ and almost 1 GPa of H_2 gas pressure. Further experiments [4, 5] proved that the equilibrium formation pressure of NiH is lower and equals 0.63 GPa at room temperature. This result, obtained by using a simple piston-cylinder apparatus initiated development of more sophisticated instrumentation and extensive exploration of metal-hydrogen systems in searching for novel hydrides. Discovery of superconductivity of PdH_x by Skoskiewicz [6] from the same group had further stimulating effect for these challenging studies. In this paper, we will review high pressure hydride syntheses with main focus on transition metals and Laves phase alloys.
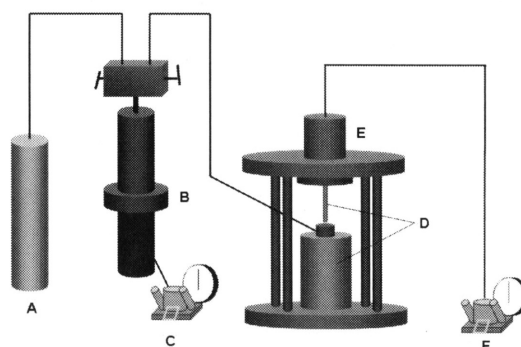
2. HIGH PRESSURE APPARATUSSES FOR HYDROGEN COMPRESSION

Figure 1. System for hydrogen pressure up to 2 GPa (H_2): (A) H_2 bottle, (B) Pressure intensifier up to 0.1 GPa (H_2) ; (C)(F) Oil pumps, (D) Piston-cylinder high pressure apparatus, (E) Hydraulic press.

The simplest system for experiments with high hydrogen pressure, designed in our laboratory is shown on Fig. 1. It is composed of H_2 bottle, pressure intensifier, hydraulic press and setup of one stage piston - cylinder apparatus.

H_2 from the bottle (usually at pressure 15 MPa) is preliminary compressed by pressure intensifier to about 0.1 GPa and then conducted through the capillary to cylinder containing samples to be investigated. Cylinder, shown in Fig. 2 [7], is made of three coaxial tubes; inner tube is made from hardened Cu-Be alloy (a hydrogen resistant material) while two outer are made from hardened high strength steel. Bottom side of cylinder is closed with a stopper locked by a plate fixed by screws. A movable piston is closing the cylinder from its upper side. Both, stopper

and movable piston are sealed with rubber o-ring and a metal ring. The temperature of this piston-cylinder apparatus can be stabilized within the range of -100 ~ 150 ℃ by using an outside heating mantle, thermometer and temperature control system. Treatment of samples at high pressure and temperatures higher than 150 ℃ (up to about 800 ℃) can be executed in a mini-furnace located in the working volume of cylinder. In such case, the cylinder must be cooled through the cooling mantle to protect it from the overheating.
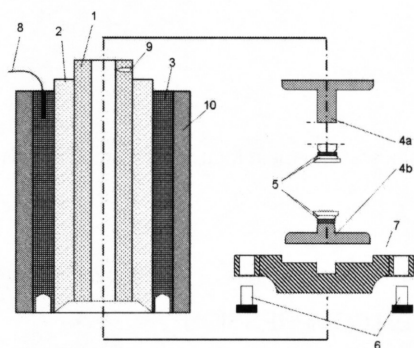

Figure 2. High pressure apparatus for H_2 pressures up to 2 GPa (H_2). (1) Cu-Be inner tube, (2)(3) high strength steel cylinders, (4a)(4b) piston and stopper; (5) sealings, (6) screws, (7) closing plate, (8) thermocouple, (9) H_2 inlet, (10) heating/cooling mantle [Ref. 7].

Due to limited strength of Cu-Be alloy, a special modification of the piston-cylinder apparatus is necessary for pressure range expanded to 3 GPa. An effective solution is two-stage construction [8]. The Cu-Be vessel is closed with a movable piston sealed by a teflon ring, initially charged with H_2 at 0.1 GPa and then placed in high strength steel (maraging steel) cylinder filled with a pressure transmitting liquid (mixture of alcohols or light hydrocarbons). Due to low friction of the teflon sealing the pressures, inside and outside of the inner Cu-Be vessel are practically equal. Therefore this inner vessel is not mechanically charged and available pressure limit depends only on the strength of the maraging steel cylinder, stopper and movable piston (both made of tungsten carbide). Electrical leads delivered to the samples located in hydrogen atmosphere in the inner vessel can be used to measure any electrical properties (resistivity, thermoelectric power,etc.).

Extension of pressure range up to ~ 9 GPa has been proposed by the group of Ponyatovskii [9] who applied a toroidal high pressure apparatus combined with an ampoule containing investigated sample and a hydride (for example, MgH_2 or AlH_3) as hydrogen source material. This hydride was separated from the

sample by a chemically inert liquid (silicone oil). After preliminary compression the hydride is decomposed and bubbles of H_2 gas go through the liquid layer to the upper part of capsule where it can react with the sample.
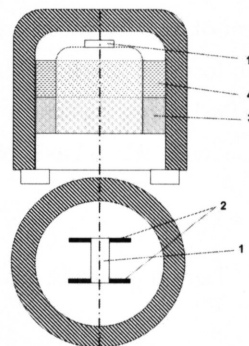
Figure 3. Ampoule for generation of hydrogen pressure up to ~ 10 GPa to be applied with a standard quasihydrostatic high pressure apparatus. (1) sample, (2) electrical leads, (3) H_2 source, (4) silicone oil. [Ref. 9].

Another approach, eliminating liquid (which can be responsible for contamination of the sample) which was proposed by Sawaoka, Wakamori and Filipek [10] is shown on Fig. 4.
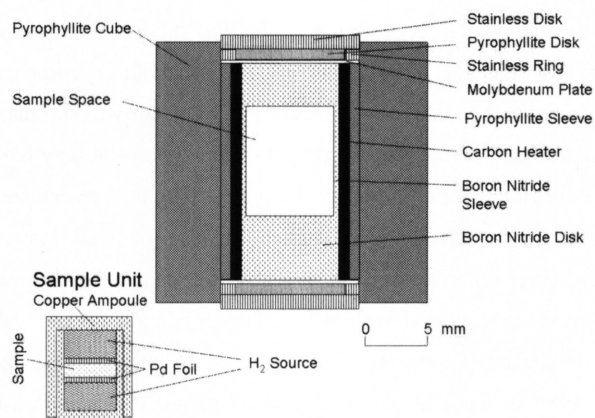
Figure 4. Cu ampoule for generation of H_2 gas pressure up to ~ 10 GPa to be applied with a standard quasihydrostatic high pressure apparatus. [Ref. 10].

They proposed a tight Cu ampoule which contains a sample disc covered from both sides by a Pd foils and placed between two plates of hydrogen source material. This "sandwich" structure can be used for syntheses of hydrides at ~ 10 GPa H_2 pressure conditions. Similar solution was proposed by Fukai [11], Yamakata [12] and Antonov [13]. The ampoules of both kinds (with or without liquids) can be used for any type of high pressure apparatus as toroidal, belt, tetragonal, six-anvils cubic press etc.
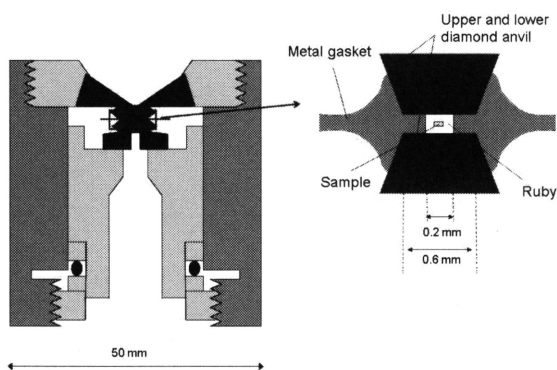
Figure 4. Schematic illustration of Diamond anvil cell (DAC).

Pressures of one order higher became available by introducing the diamond anvil cell (DAC) [14]. Charging with hydrogen can be done by closing liquid (or solid) hydrogen [15] or precompressed H_2 gas [16] in the space between two diamond anvils. This kind of apparatus has been used for study of EOS (Equation of State) and phase transitions of pure H_2 [15, 17-19] as well as for syntheses of hydrides [12, 20-24]. In extremely high pressures, it is necessary to consider possible chemical reactions which might occur in such conditions. Otherwise observed phenomena can lead to wrong conclusions as reported in Reference [25] describing the case of "metallization of SiH_4" which in fact was related to formation of PtH in reaction of Pt gasket with hydrogen generated during SiH_4 decomposition.

3. HYDRIDES OF TRANSITION METALS

Since this paper concerns only hydrides formed at high hydrogen fugacity, we will not discuss here the hydrides of such metals as Pd, V, Ti, Zr or Nb which easily react with hydrogen even at low pressure.

3.1 Ni and Ni-based alloys

The NiH, unstable at 25 °C has been discovered in 1959 by Baranowski and Smialowski [26] during electrochemical charging of Ni by H. The formation of NiH is accompanied by a discontinuous increase of the lattice parameter of *fcc* Ni by about 6 %. Decomposition pressure of the NiH at 25 °C was estimated at 0.34 GPa [27]. Due to absorption/desorption hysteresis, it was expected that synthesis of NiH from metallic Ni foil and gaseous H_2 would require a higher pressure. Aiming at synthesis of NiH directly from elements the first equipment for hydrogen compression up to 1 GPa (H_2) range has been designed and successfully applied. Formation pressure of NiH was determined

as 6.3 GPa (H_2) at 25 °C [4, 5] what confirmed existence of a very large hysteresis between absorption and desorption branches of the isotherm. This synthesis of NiH - the first high pressure hydride was a milestone in the studies of metal-hydrogen systems. It opened the way for syntheses and investigation of properties of a number of novel hydrides. Recently several review articles on formation, kinetics, magnetic and transport properties of Ni and Ni-based alloys were published [28, 29].

Formation of hydride phases can be traced by taking X-ray diffraction (XRD) patterns (directly *in situ* in a DAC) or by measuring electric resistivity or/and thermoelectric power (TEP) as a function of H_2 pressure. Determination of these properties gives also valuable information about influence of hydrogen on electronic properties of investigated alloy. For instance, according to approach of Mott [30] and its improved versions [31] the net diffusion thermoelectric power depends, approximately, on the derivative of the density of states on energy at the Fermi level. Studies of the influence of hydrogen on the thermopower at 25 °C in different <u>Ni</u>Me alloys (where Me stands for alloying elements) revealed three different behaviors during formation of a hydride:

i) Increase of TEP from negative values to ~ 0 μV/K, thus value characteristic for pure Cu, the next element after Ni in the *3d* series. This positive change of TEP during formation of hydride occurs for pure Ni and for Ni alloyed with *p* elements (Al or Si) or such *d* elements as Cu or Fe, which only slightly change the band structure of Ni [32-36].

ii) It is interesting that TEP changes during hydride formation in <u>Ni</u>Co alloys differ from those of <u>Ni</u>Fe [37]. The TEP of $Ni_{95}Co_5H_{1.0}$ is almost the same as that of parent alloy (~ -22 μV/K) while for $Ni_{90}Co_{10}H_{0.9}$ it drastically falls down approaching to -40 μV/K. Let us remark that NiH, in which electrons from hydrogen fill up the holes in *s/p*- and *d*-band, has electronic structure similar to that of Cu or Au. This can suggest that tendency observed in $(\underline{Ni}Co)H_x$ has similar origin as in <u>Cu</u>Co or <u>Au</u>Co for which the giant negative TEP were attributed to the Kondo effect. The minima of TEP for Fe doped Cu or Au are not as deep as for Co doping. Also for Fe, these minima are located at low temperature while for Co impurities the Kondo temperature can be as high as 25 °C. The large negative TEP of $(\underline{Ni}Co)H_x$ can be therefore explained in terms of Kondo systems with high temperature T_K just like <u>Cu</u>Co or <u>Au</u>Co.

iii) It is known that Ni substituted by such *3d* transition metals as Ti, V or Cr, has anomalously large change of TEP (from great

negative to high positive values) with increasing concentration of the substitute. This is related to the presence of impurity virtual bound state (VBS) at the Fermi level [38]. Now, during hydrogenation, the change of TEP can be positive, none or negative depending on the initial TEP value of the parent alloy [39]. As can be seen on Fig. 5, the formation of hydrides evidently compensates the changes of TEP resulted from doping of Ni by Ti, V or Cr. In spite of very different initial TEP values (from about -20 μV/K to about + 25 μV/K) of these alloys, their hydrides have almost the same small positive value of TEP, just as pure NiH.
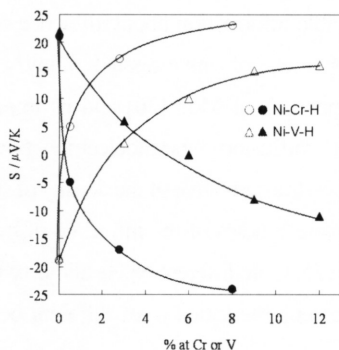
Figure 5. Thermoelectric power S_{Me} of H-free alloys (open symbols) and its change ΔS during hydride formation (black symbols) as functions of Cr or V content in their alloys with Ni [Ref. 39].

Qualitative explanation of the observed behavior can be given using simple model illustrating changes in the electronic structure as shown in Fig. 6. Fig. 6a shows the electronic structure of Ni or Ni alloyed with elements which cause only small changes in the electronic structure. During formation of hydride in these alloys, the protons locate in the interlattice spaces of the Ni while electrons fill up the empty states in the d band (Fig. 6b) just like in Cu - the transition metal with completely filled $3d$-band. At the same time, the Fermi level moves towards higher energies, ferromagnetism is lost [28, 39] and the TEP approaches the value characteristic of Cu.

Appearance of the VBS near the Fermi level in Ni alloyed with Cr, V or Ti (Fig. 6c) drastically changes the TEP value but this change is cancelled with formation of hydride when Fermi level is shifted to energy higher than the position of VBS peak. Consequently the TEP values approach the TEP of NiH independently of the initial TEP value of the parent alloy.

Similar mechanism can explain also properties of PdRu-H, PdRh-H and PdIr-H systems [40] being consistent with the "periodic effect" defined by Demangeat and Gautier [41].
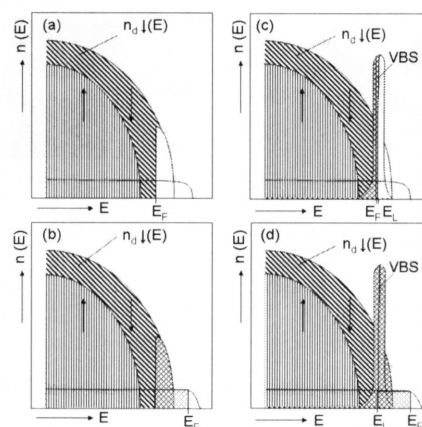
Figure 6. Schematic illustration of the band structure changes during hydride formation in Ni and in Ni alloys in which the VBS appears near the Fermi level: (a) pure Ni, (b) NiH, (c) H-free VBS alloy; (d) hydride of the VBS Ni alloy [Ref. 39].

3.2 Other transition metals hydrides.

Soon after the NiH, the high H_2 pressure technique developed in IPCh PAS has been successfully applied for synthesis of CrH [42] and *hcp* MnH_x [43]. Further progress has been done by Russian group who synthesized hydrides of Co, Fe, Mo, Tc, Rh and Ru [13, 44-50]. Recently direct syntheses of CuH [22] and PtH [51] in hydrogen charged DAC beyond 10 GPa (H_2) have been also reported. Those transition metals hydrides which direct synthesis from metal and gaseous H_2 requires of "GPa-class" high H_2 pressure are collected in Table 1. However, two hydrides (CrH and NiH) can be prepared alternatively by electrochemical method. On the other hand, according to our knowledge, formation of hydrides of W, Os or Ir has never been reported.

Mn-H system is unique, in particular. The *hcp* MnH_x, which is stable at ambient conditions, was the first really "high pressure hydride" as other methods of its preparation (like in the case of NiH or CrH) were not known. Also, among hydrides listed in Table 1, the transformation from αMn (*bcc* phase with 58 Mn atoms in a unit cell) into *hcp* or *fcc* hydride is the most complicated process. It is interesting to note that also the presence of Mn in RMn_2 (R = Y, Er, Ho, Dy, Ho, Gd) Laves phase alloys is responsible for dramatic restructurization of the parent metal lattices (C14 or C15 types) during the RMn_2H_5 hydrides formation [56, 57]. This behavior suggests existence of a very unusual, specific interaction between Mn and H atoms.

During the exposure of Mn into gaseous H_2 at high pressure and high temperature conditions, two different hydrides can be obtained:

i) the *hcp* MnH$_x$ which was synthesized by Krukowski and Baranowski [43]. The volume of *hcp* MnH$_x$ calculated per Mn atom ranges from 1.335×10^{-2} nm^3 to 1.376×10^{-2} nm^3 when x increases from 0.65 to 1.0.

ii) the cubic (*fcc* metal lattice) MnH$_x$, which was observed occasionally by Krukowski in the *hcp* phase as an impurity. Later, it was synthesized as a single phase by Fukai *et al.* [11] and Filipek *et al.* [58].

A weak ferromagnetism in the *hcp* MnH$_x$ has been reported by Belash *et al.* [59]. This could indicate presence of a small amount of hypothetical ferromagnetic *fcc* Mn structure predicted theoretically [60]. In this aspect, two questions would appear:

1) Does a ferromagnetic MnH$_x$ exist?

2) Does ferromagnetic Mn predicted theoretically exist?

In order to answers these questions, one *hcp* (Sample 1) and two samples of *fcc* MnH$_x$ (Samples 2 and 3) with possibly large lattice parameters were prepared [53].

Sample 1; *hcp* MnH$_{0.84}$ ($a = 0.2700$ nm and $c = 0.4378$ nm).

Sample 2; non-magnetic; *fcc* MnH$_{0.64}$ ($a = 0.3827$ nm).

Aiming at increase of the lattice parameter above the critical 0.384 nm value, synthesis of hydride was performed in H$_2$ contaminated with a small amount of N$_2$. Product of this synthesis was Sample 3; *fcc* MnH$_{0.30}$N$_{0.08}$ with lattice parameter $a = 0.3856$ nm which showed ferromagnetic properties supporting the theoretical prediction.

Possibility of pressure induced phase transition has been checked by using DAC technique for *hcp* MnH$_{0.84}$ and for both *fcc* hydrides. The *hcp* structure of MnH$_{0.82}$ sample was stable up to the 25 GPa pressure limit while *fcc* MnH$_{0.64}$ transformed irreversibly at 8 GPa into *hcp* modification. In spite of larger molar volume and smaller occupancy of interstitial sites than *fcc* MnH$_{0.64}$, the ferromagnetic sample *fcc* MnH$_{0.30}$N$_{0.08}$ showed only continuous reduction of volume with pressure, without structural changes up to 25 GPa. The ferromagnetism of this *fcc* phase remained also after annealing at 523 K in vacuum. These conditions were sufficient for removing interstitial atoms (H and N) but temperature was still too low for restructurization of the metastable ferromagnetic *fcc* Mn ($a = 0.385$ nm; 0.13 μ_B/at Mn). However, without stabilizing effect of H and N interstitial atoms the *fcc* Mn framework has collapsed at 9 GPa of hydrostatic pressure. However, in this case instead of the *fcc* → *hcp*, we found transition into the α-Mn.

With the exception of MnH$_x$, CrH and TcH$_x$, all other hydrides given in Table 1 are unstable and rapidly decompose at ambient conditions. Therefore their properties must be measured *in situ*

under pressure or at low temperatures after taking sample out from the high pressure apparatus. It should be also noticed that the amount of hydride to be prepared is inversely proportional to the pressure required for the synthesis. For instance, dimensions of samples compressed in DAC are of several microns only. For these reasons, studies on hydrides of Fe, Pt or Os, are valuable for basic research or for understanding processes taking place in the core of planets. However, it is hard to expect that these "exotic" hydrides would find any practical application.

Table 1. Hydrides of transition metals synthesized under high H$_2$ pressure.

Hydride	Structure and lattice constant [nm]	Formation conditions	Ref.
*CrH	*hcp* $a = 0.2717, c = 0.4436$	1.815 GPa (423 K)	42
*MnH$_{0.65}$	*hcp* $a = 0.2668, c = 0.4324$	0.74 GPa (577 K)	43
*MnH$_{0.82}$	*hcp* $a = 0.2692, c = 0.4362$	1.30 GPa (577 K)	43
*MnH$_{0.41}$	*fcc* $a = 0.3776$	2 GPa (1073 K)	52
*MnH$_{0.64}$	*fcc* $a = 0.3827$	1.2 GPa (800 K)	53
*MnH$_{0.3}$N$_{0.08}$	*fcc* $a = 0.3856$	1.0 GPa (600 K)	53
FeH$_{0.95}$	*dhcp* $a = 0.269, c = 0.879$	3.5 GPa (298 K)	12
FeH$_{0.8}$	*hcp* $a = 0.2686, c = 0.4380$	6.7 GPa (523 K)	46
FeD$_{0.42}$	*hcp* $a = 0.2583, c = 0.4176$	9.2 GPa (623 K)	45
CoH$_{0.5}$	*hcp* $a = 0.2579, c = 0.4162$	6.5 GPa (500 K)	44
CoH	*fcc*	7.0 GPa (623 K)	44
NiH	*fcc* $a = 0.373$	0.62 GPa (298 K)	3
CuH$_{0.4}$	*fcc* $a = 0.37$	14.4 GPa (298 K)	22
MoH	*hcp* $a = 0.2937, c = 0.4758$	3.5 GPa (400K)	47
*TcH$_{0.5}$	*Hcp* $a = 0.2801, c = 0.4454$	0.7 GPa (673 K)	48
TcH$_{0.7}$	*hcp* $a = 0.2838, c = 0.4465$	2.0 GPa (673 K)	48
RuH$_{0.03}$	*hcp*	9.0 GPa (523 K)	49
RhH	*fcc* $a = 0.4010$	4.0 GPa (523 K)	13
RhH	*fcc* $a = 0.401$	3.8 GPa (298 K)	21
W	*Hydrides are not formed up to 9 GPa.*		54
ReH$_{0.38}$	*hcp* $a = 0.2801, c = 0.4440$	10.2 GPa (298 K)	50
Os	*Hydrides are not formed up to 9 GPa.*		54
Ir	*No hydrides are not formed up to 9 GPa.*		54
PtH	*hcp* $a = 0.2773, c = 0.4713$	27 GPa (298 K)	51
AuH$_{0.43}$	*Rhombohedral*	2.8 GPa (625 K)	55

*Hydrides stable at ambient conditions

4. HYDRIDES OF LAVES PHASE ALLOYS

Recently we started systematic search of novel "high pressure" hydrides in alloys considered as non-hydride forming materials as well as in those already explored at moderate hydrogen pressure conditions.

According to our expectations, the treatment of Laves phase alloys by high hydrogen pressure resulted in syntheses of number of novel hydrides. Surprisingly, they are often stable in ambient conditions in contrast to mostly unstable hydrides discussed in the previous chapter.

Three groups of Laves phase hydrides discovered under high hydrogen pressure will be briefly characterized below.

4.1 Hydrides formed with isotropic lattice expansion

$ZrFe_2H_4$ and $ZrCo_2H_2$ which form at 100 ℃ from parent C15 Laves phase compounds at 0.3 and 1 GPa (H_2) pressures respectively [61, 62] have expanded C15 lattice of parent compounds. $ZrFe_2H_4$ is not expensive and contains relatively high amount of hydrogen so it can be considered as possible hydrogen storage material. Its disadvantage is that it can burn in contact with air but in inert atmosphere or after poisoning its surface it is stable and can be stored long time without decomposition. The $ZrCo_2H_2$ is unstable and in ambient conditions it decomposes within a few hours. Hydrides of pseudobinary $Zr(Fe_xCo_{1-x})_2$ compounds are formed in whole composition range and the "x" value controls stability and other properties of hydrides of these pseudobinary alloys [63].

4.2 Hydrides formed with anisotropic lattice expansion

The C15 cubic YFe_2, $ErFe_2$ and $HoFe_2$ at low or moderate pressures can form hydrides up to about 4.2 H/f.u. Below this concentration several hydrides with different crystal structure can appear with expansion of crystalline lattice proportional to the hydrogen content.

At high pressure near 1.0 GPa (H_2) and 100 ℃ the RFe_2 (R = Y, Er, Ho) Laves phase compounds change into non magnetic isostructural orthorhombic hydrides such as YFe_2H_5, $ErFe_2H_5$ and $HoFe_2H_5$ [63–65]. These hydrides are stable and can be stored long time at room temperature.

4.3 Hydrides formed with radical restructurization of the metallic lattice

A very unique group, found only for RMn_2 intermetallics (R = Y, Gd, Dy, Ho, Er) are isostructural $Fm-3m$ RMn_2H_6 hydrides

[56, 57, 66-68]. These kinds of hydrides, formed independently of the structure of the parent alloy (C14 or C15) were never obtained directly from Laves phase compounds. It seems that presence of manganese is crucial for their formation. As in the case of pure αMn also in RMn_2 Laves phases the "high pressure" hydrides are formed with very radical restructurization of the crystalline lattice. Let us remind that hcp and fcc MnH_x formed under high pressure are stable at ambient conditions. Also the RMn_2H_6 $Fm-3m$ hydrides are very stabile. Their stability is related to different type of bonding comparing all other Laves phase based hydrides which are of the interstitial type. In contrast to them, the RMn_2H_6 $Fm-3m$ hydrides group can be classified as complex hydrides in which one Mn atom, located at $4a$ site is surrounded by six H atoms forming a complex anion,

Figure 7. Changes of structure during formation of high pressure hydrides from Laves phase compounds.

Table 2. Laves phase based hydrides synthesized under high hydrogen pressure.

Hydride	Structure and volume expansion ($\Delta V/V_0$ [%])	Lattice parameters [nm]	Ref.
*$ZrFe_2H_4$	Cubic, Fd-3m (22.8)	a = 0.7637	61, 62
$ZrCo_2H_2$	Cubic, Fd-3m (14.0)	a = 0.7267	61, 62
*YFe_2H_5	Orthorhombic, Pmn21 (28.9)	a = 0.54369(1) b = 0.58499(1) c = 0.80822(2)	63 - 65
*$ErFe_2H_5$	Orthorhombic, Pmn21 (30.6)	a = 0.54242(1) b = 0.57933(1) c = 0.80091(1)	63 - 65
*$HoFe_2H_5$	Orthorhombic, Pmn21 (28.9)	a = 0.54161(3) b = 0.57855(3) c = 0.80090(5)	63
*YMn_2H_6	Cubic, Fm-3m (33.3[a])	a = 0.67090(2)	56, 68
*$ErMn_2H_6$	Cubic, Fm-3m (42.00[b])	a = 0.66797(2)	63, 66
*$DyMn_2H_6$	Cubic ,Fm-3m (38.98[a])	a = 0.67172(2)	57, 63
*$HoMn_2H_6$	Cubic, Fm-3m (38.77[a])	a = 0.66800(2)	57, 67
*$GdMn_2H_6$	Cubic, Fm-3m	a = 0.67516(2)	57, 63

*Hydrides stable at ambient conditions. [a] Calculated with respect to C15 parent; [b] calculated with respect to C14 parent.

while the second Mn occupies *8c* site statistically together with an R atom. Three groups of Laves phase based hydrides are listed in the Table 2.

5. CONCLUSIONS

Application of high hydrogen pressure for studies of hydrogen - metal systems resulted in syntheses of number of novel hydrides and understanding of interaction between hydrogen and metals. In spite of preparation under very high pressures, several hydrides, surprisingly, are stable or very stable at ambient conditions. It seems that, in spite of very intensive research continued from early 1970s, the exploration of this field can still bring discoveries of further novel hydrides and unexpected, surprising phenomena.

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