

METAL HYDRIDES AT HIGH PRESSURE

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Abstract

The influence of high pressure on properties of metal hydrides is investigated poorly. At the same time metal hydrides are rather interesting objects for the high pressure chemistry and physics. First of all it is connected with a considerable metal matrix volume increase while hydriding. Due to this the application of the high pressure technique gives the possibility of synthesis of more dense modifications, of new hydrides with large hydrogen capacity. The present work summarises the results of the investigations of binary and heterometallic hydrides and of new hydrides synthesis.

Introduction

The influence of high pressure on the properties of metal hydrides is studied rather insufficiently. However, metal hydrides are extremely interesting objects for the chemistry and physics of high pressure. First of all it is connected with the fact that while hydride formation considerable changes of metal matrix volume take place. Hence, the use of the high pressure technique provides the possibility of obtaining more dense modifications and synthesising new hydrides with increased hydrogen capacity. Considerable contributions to this field of study were the works of several groups headed by B.Baranowsky, E.Ponyatovsky, V.Somenkov, W.Bronger and Y.Fukai. The present work generalise the results of investigations of the influence of high quasihydrostatic pressure (HQHP) and high gaseous hydrogen pressure (HGHP) on the transformations of binary and heterometallic hydrides and on the synthesis of new hydride.

Hydrides of Light Metals

Hydrides of alkali, earth-alkali metals, boron, aluminium and their complexes are well known and find a wide application in inorganic and organic chemistry. Firstly it is connected with high hydrogen content and their reduction properties (for example hydrogen mass contents in BeH_2 and AlH_3 is 18% and 10 % respectively). A series of works dealing with the investigation of alkali metal hydride behaviour at high pressure appeared in the early 80-s [1-6]. The analysis of the obtained results confirms that for the potassium, rubidium and caesium hydrides the transition from NaCl structure type to CsCl structure type takes place at 40, 18.8-22 and 7.4-12 kbar respectively and the transition pressure values decrease with the increasing ionic radius of metal. Corresponding elementary cell volume change undoubtedly gives evidence of a large value of compressibility of hydride-ion. The calculated values of phase transition pressure for lithium and sodium hydrides are considerably higher.

The study of phase transitions of beryllium, magnesium and aluminium hydrides at HQHP conducted together with K.N.Semenenko, B.M.Bulychev and A.L.Dorosinsky resulted in following major facts.

Beryllium hydride BeH_2 synthesised by different methods is formed as an amorphous powder ($\rho_{\text{pikn}} = 0.57 \text{ g/cm}^3$). At 50-70 kbar and 400-600 $^\circ$ it crystallises with the increase in density by approx. 30%. This crystal form of BeH_2 is metastable as the heating up to 240 $^\circ\text{C}$ at normal pressure leads to the reformation of the amorphous hydride. Absolutely new feature – the effect of melting at high pressure for beryllium hydride was discovered in [7].

Magnesium hydride $\beta\text{-MgH}_2$ obtained by direct hydriding of metal crystallises in TiO_2 type ($\rho_r = 1.42 \text{ g/cm}^3$). At HQHP two more modifications are formed – $\alpha\text{-MgH}_2$ isotypic to $\alpha\text{-PbO}_2$ and $\gamma\text{-MgH}_2$ [8-10].

As follows from Fig.1 in α - and β -modification of MgH_2 magnesium nearest neighbours stay the same and the difference is only in the location of chains of octahedra. Possible this account for the extremely small increase in density for high pressure modifications ($\rho_r = 1.43 \text{ g/cm}^3$). We have not found similar transformation of CaH_2 and BaH_2 at HQHP.

Varying the methods of synthesis of aluminium hydride allowed to obtain five modifications of this compound – α -, β -, δ -, σ - AlH_3 . Fig.2 shows that for all of them the differences in structure come out of the different methods of $[\text{AlH}_6]$ -octahedra packing.

The most stable of these modifications is $\alpha\text{-AlH}_3$ ($\rho_r = 1.47 \text{ g/cm}^3$). Possibly this is determined by the fact that all other modifications of aluminium hydride transform to $\alpha\text{-AlH}_3$ at HQHP. Despite that the structure of $\alpha\text{-AlH}_3$ is rather friable it was not possible to synthesise the modification with higher packing coefficient. Analogous results were obtained in a series of works at HQHP as well as at HGHP [7, 11-13].

Number of publications on synthesis and phase transformations of heterometallic hydrides at HQHP is rather limited. The possibility of synthesis of new hydrides with antiperovskite structure in the LiH-CaH_2 (BaH_2 , EuH_2 , ScH_2 , YH_2 , CeH_2 , LaH_2 , TiH_2 , VH_2) systems at pressures up to 70 kbar and temperatures up to 900 $^\circ\text{C}$ was studied in [14]. It was stated that under these conditions only known complex LiBaH_3 and LiEuH_3 hydrides are formed. Despite the fact that according to crystal conceptions (for ABO_3 $R_A + R_B = t\sqrt{2(R_B + R_O)}$) for systems with ScH_2 , YH_2 , CaH_2 and LaH_2 $t \rightarrow 0.9$ the formation of heterometallic was not found. Also no new compounds were obtained for $\text{MgH}_2\text{-TiH}_2$ (VH_2) systems. Meanwhile for complex LiBH_4 and LiAlH_4 a series of polymorphic transformation was detected [15-18].

It should be noted that if the fact of $\alpha\text{-LiAlH}_4$ ($\rho_r = 0.917 \text{ g/cm}^3$) \rightarrow $\beta\text{-LiAlH}_4$ ($\rho_r = 1.02 \text{ g/cm}^3$) transition does not evoke objections of different investigators, the formation of $\gamma\text{-LiAlH}_4$ is not confirmed by [19]. In similar high pressure conditions NaAlH_4 does not undergo phase transformations. Complex hydrides M_3AlH_6 ($\text{M} = \text{Li, K, Na}$) which crystal structure is composed of octahedral ions $[\text{AlH}_6]^{3-}$ and alkali metal cations form denser β -modifications at high pressure [20-21].

Use of high pressure technique allowed to synthesise a series of heterometallic hydrides containing II group metals. For Ca-Ni (Co)-H_2 systems the existence of CaNiH_3 and CaCoH_3 of perovskite structure type was supposed [22]. The formation of new heterometallic hydrides was also stated for Mg-Mo-H_2 and Mg-Mn-H_2 systems. It was noted that Mg_3MnH_7 is isostructural to Mg_3ReH_7 and its crystal structure can be described by a regular location of octahedra $[\text{MnH}_6]$ [23].

Hydrides of Rare-Earth Metals

From the works on the synthesis and phase transformations of hydrides of rare-earth metals and intermetallic compounds on their base one can mark following major results [24-31]. One of the obvious achievements of the high pressure method is the synthesis of scandium trihydride. For dihydrides of scandium, yttrium, lanthanum, ytterbium, europium, terbium, samarium, dysprosium, neodymium, gadolinium and erbium phase transitions at high pressure are not characteristic. For trihydrides a phase transition connected with the transfer from hcp to fcc structure.

The investigation of the behaviour of rare-earth intermetallic compounds and their hydrides at high pressure – is relatively poor researched field of hydride chemistry. In the first works [32-35] the representatives of RT_2 , RT_3 and RT_5 types were studied. The investigations showed that application of high pressure leads to the increase in content of the absorbed hydrogen by 1.5-2 times. For example, $LaCo_5H_9$, $CeCo_5H_{7.3}$, $YNi_5H_{3.5}$, $LaPt_5H_{4.6}$, $ErCo_3H_{5.5}$, $DyFe_2H_7$ were obtained. At the same time the stability of metal matrix at high hydrogen pressure decreases – disproportionation of $LaNi_5$ and $LaCo_5$ begins even at 300-350°C [34]. A detailed study of hydrogen interaction with intermetallic RT_5 and RT_3 compounds was performed in [37-39]. The absorption-desorption isotherms were obtained in the wide pressure and temperature range thermodynamical parameters of reactions were calculated. It is worth mentioning that in the case of $CeNi_3$ and $ErNi_3$ compounds rather peculiar hydride at high pressure properties were found. As follows from Fig.3 for these compounds it became possible to realise the assumption about additional hydrogen implantation into metal sublattice of hydride synthesised beforehand. Another interesting property also to be noted is that although these hydrides form at very high hydrogen pressure, at normal conditions the hydrides of maximum composition $RNi_3H_{5.6}$ are rather stable and desorb hydrogen very slowly while storage.

The phase transition in HQHP conditions was found only for one hydride – $ErNiH_{3.7}$ [40]. Closely related $LaNi$ and $CeNi$ in similar conditions undergo the disproportionation forming RH_3 and R_3Ni_7 .

Hydrides of Transition Metals

The study of behaviour of hydrides of copper and zinc at high pressures (56-77 kbar) showed that even at these extreme conditions they do not appear to have the stability regions and decompose to elements [41-42].

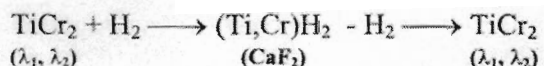
The major number of works studying the influence of high pressure on the transformations of transition metal hydrides deal with titanium hydride phases [43-49]. Summarising the obtained result it is possible to conclude that a series of transformations can be found for the compositions TiH_x ($x = 0.6-1.3$) at high pressure – transfer to superconducting state and synthesised phase with hydrogen occupying the octahedral interstices. The superconductivity phenomenon was also found for thorium and palladium hydrides [49-50].

For titanium dihydride the polymorphism cause by high pressure does not occur [51] and at HGHP the existence of phases with $H/Ti > 2$ is supposed [52].

$Ti_4FeH_{8.8}$ hydride phase being a solution of iron in titanium dihydrides undergo disproportionation to iron and titanium hydride at HQHP [53].

The data volume on behaviour of intermetallic hydrides at high pressure is also rather small. For ZrV_2 and HfV_2 the superconductive transformation was found at HQHP [54]. For $ZrCo$, Zr_2Co and $ZrNi$ no pressure phase transformation was found – at high pressure and temperature the disproportionate [55-57] takes place.

Behaviour of $TiMn_2$ and $TiCr_2$ Laves phases at HGHP was studied in [58-61]. The following results are worth noting. A considerable solubility of hydrogen in $TiMn_2$ after activation starts only at 50 atm and the formation of hydride $TiMn_2H_3$ takes place at hydrogen pressure over 700 atm (Fig.4). In consecutive absorption-desorption cycles the hysteresis loop for this system changes from both sides, namely the pressure values of absorption decrease and desorption ones – increase. The results of investigation of decomposition of $(Ti,Cr)H_2$ hydride phase synthesised from $TiCr_2$ at HGHP can be presented by following scheme:



It was stated that the metal sublattice of the hydride performs an "structure memory" effect so that its structure after hydrogen desorption transforms to the starting one (λ_1 or λ_2) used for hydride synthesis.

Application of high pressure allowed obtaining for the first time new hydrides $ZrRuH_{2.2}$ and $HfRuH_{3.6}$ having superconductive properties. Still the structures of these hydrides need more precise definition [62-63].

Additional absorption of hydrogen at HGHP was found for intermetallic compounds Zr_2Pd , Hf_2Pd and Hf_2Cu resulting in formation of $R_2TH_{5.5-6}$ hydrides characterised by a considerable rhombic distortion of the crystal lattice [64].

Conclusion

New information can possibly be obtained by applying the HQHP and low temperature. Most prospective materials for these studies are the intermetallic hydrides with clearly defined anisotropic lattice distortion. This assumption is also valid for the investigations, performed under HGHP.

The comparative analysis of results obtained by investigation of intermetallic hydride behaviour at high pressure allows to draw some conclusions. Due to the larger strength of both metallic and hydrogen sublattice phase transitions for majority of structure types can be expected at pressures higher than those applied up to now.

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