PHYSICS OF METAL HYDRIDES

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Keywords: Crystal structures, Thermodynamic properties, Electronic structures, Ternary hydrides.

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Summary

Physical properties of ternary hydrides are briefly reviewed. Thermodynamic properties of metal (alloy) hydrogen systems are described. Crystal structure which is refined for their deuterides is demonstrated for typical examples. The electronic structure of metal hydrides are discussed and that of $LaNi_5$ is shown in detail.

1. The Stability of Hydrides

Hydrides which are used for hydrogen storage and electrodes are usually ternary hydrides. Therefore, discussion in this chapter is focused on ternary hydrides which are normally formed by hydrogenation of intermetallic compounds or solid solution of more than two metallic elements. The principle of formation of ternary hydrides is essentially the same as that of hydrides of pure metals although ternary hydride systems are much more complicated to understand theoretically.

Because of stability of hydrides is a most important quantity, empirical rules have been proposed to predict the stability of a given alloy-hydrogen system. Miedema's rule of reversed stability is the most popular one. They proposed the following relation between hydride stability and alloy stability.

$$DH\left(AB_nH_{2m}\right) = DH\left(AH_m\right) + DH\left(B_nH_m\right) - DH\left(AB_n\right) \tag{1}$$

In this model the enthalpy effects are considered to arise from the effective areas of contact between the composing elements. In the most simple cases the enthalpy of formation of a ternary hydride is the difference between the two hydride formation enthalpy of the component metals and that of alloy formation enthalpy. Generally, the first term on the right-hand side of Eq. (1) is negative and the largest in absolute value

whereas the second term is small and may be positive. Therefore, the sum of the first and second terms are almost of equal size for a given class of alloy systems. This means that if the third term of the right hand side of Eq. (1) becomes more negative (more stable), the left-hand side becomes more positive (more unstable). In the case of LaNi$_5$, relation (1) becomes:

$$DH(LaNi_5H_6) = DH(LaH_3) + DH(Ni_5H_3) - DH(LaNi_5) \tag{2}$$

The values of each term of the right hand side are –252, +4, and +168 kJ/mol alloy. The left-hand side of Eq. (2) is then calculated to be –80 kJ/mol alloy (–27 kJ/mol H$_2$), which agrees well with the observed value, –32 kJ/mol H$_2$. LaCo$_5$ is one of the same series alloys to LaNi$_5$ and is less stable than LaNi$_5$. It clearly shows that these AB$_5$-type hydrides obey the rule of reversed stability.

A similar relation is also found in the Mg$_2$XH$_y$ (X = Fe, Co and Ni) systems. Mg$_2$Fe and Mg$_2$Co alloys do not exist but their hydrides were prepared using the mechanical alloying or sintering techniques. Therefore, Mg$_2$Fe and Mg$_2$Co alloys are less stable than Mg$_2$Ni. The observed hydrogen equilibrium pressures of Mg$_2$FeH$_x$ and Mg$_2$CoH$_x$ are lower than that of Mg$_2$NiH$_x$ at the same temperature. In other words, the hydrides of Mg$_2$Fe and Mg$_2$Co are more stable than that of Mg$_2$Ni. This means that less stable alloys form more stable hydrides.

2. Crystal Structures of Metal hydrides

Table 1 lists the crystal structure parameters of selected alloys and their hydrides which are representative of each structural group or have interesting features in their crystal structures. (Note: practically crystal structure is refined for the deuterides. From Table 1 it can be found that the crystal structure changes upon hydride formation are mainly expansions of the unit cells. With hydrogenation the expansion of the lattice is generally in the range of 2–3 Å^3/H atom. Structural changes of the metal sublattices are reported for some systems, such as TiFe, Mg$_2$Ni, CaNi$_5$ and LaNi$_5$. When hydrogen occupies the interstitial sites, deformation of the lattice occurs. A typical example of the metal sublattice deformation is found in the CaNi$_5$-H$_2$ system. There are four hydride phases in this system, which was derived from an in-situ X-ray diffraction method. Hydrogen solid solution phase is the a-phase. The b-phase is found near the composition of CaNi$_5$H$_1$ and has the most deformed orthorhombic structure. The g-phase (CaNi$_5$H$_5$) is also orthorhombic but the deformation of the metal sublattice becomes close to the original hexagonal one. This phase has a wide single-phase region in the pct isotherms. The d-phase is the full hydride phase (CaNi$_5$H$_6$) and the crystal structure comes back to a hexagonal one which is the same as the alloy. It has been found that the structural changes upon hydride formation consist mainly of deformations of the metal sublattice and do not necessarily involve drastic changes in the arrangement of metals.

LaNi$_5$ P6/mmm a = 5.017 La 1a Furrer et al (1978)
c = 3.986 Ni 2c
Ni 3g
LaNi$_5$D$_7$ P63mc a = 5.388 La 2a Thompson et al. (1986)

c = 8.599 Ni1 2b z = 0.012
Ni2 2b z = 0.012
Ni3 6c x = 0.5, z = 0.203
D1 2b z = 0.348
D2 2b z = 0.348
D3 6c x = 0.153, z = 0.250
D4 6c x = 0.153, z = 0.250
D5 6c x = 0.5, z = 0.0
$LaNi_4Al$ P6/mmm a = 5.064 La 1a Percheron-Guégan et al. (1980)
(X-ray data) c = 4.070 Ni1 2c
Ni2 3g
Al 3g
$LaNi_4AlD_{4.8}$ P6/mmm a = 5.313 La 1a Percheron-Guégan et al. (1980)
(neutron data) c = 4.242 Ni1 2c
Ni2 3g
Al 3g
D1 12 n x = 0.471, z = 0.103
D2 6m x = 0.137
$Ti_{1.2}Mn_{1.8}$ P63/mmc a = 4.862 Ti+Mn 2a Fruchart et al (1984)
c = 7.969 Ti 4f z = 0.439
Mn 6h x = 0.833
$Ti_{1.2}Mn_{1.8}D_{3.1}$ P63/mmc a = 5.271 Ti+Mn 2a Fruchart et al. (1984)
(at 240K) c = 8.579 Ti 4f z = 0.442
Mn 6h x = 0.826
D1 24l x = 0.040, y = 0.343, z = 0.552
D2 12k x = 0.462, z = 0.625
D3 6h x = 0.451
D4 6h x = 0.202
$ZrMn_2$ P6₃/mmc a = 5.035, c = 8.276 Didisheim et al. (1979)
a = 5.036, c = 8.271 van Essen et al. (1980)
$ZrMn_2D_{3.0}$ P63/mmc a = 5.391 Zr 4f z = 0.066 Didisheim et al (1979)
c = 8.748 Mn1 2a
Mn2 6h x = 0.836
D1 24l x = 0.042, y = 0.325, z = 0.562
D2 12k x = 0.456, z = 0.632
D3 6h x = 0.463
D4 6h x = 0.202
TiFe Pm3m a = 2.9789 Fe 1a Thompson et al. (1989)
Ti 1b
$TiFeD_{1.9}$ Cmmm a = 7.029 Fe 4i y = 0.2887 Fischer et al. (1987)
b = 6.233 Ti 4h x = 0.223
c = 2.835 D1 4e
D2 2c
D3 2a
Mg_2Ni P6₂22 a=5.216 Ni1 3b Schefer et al. (1980)
C= 13.20 Ni2 3d
Mg1 6f z = 0.1149
Mg2 6i x = 0.1635

Mg_2NiD_4 C2/c a = 14.342 Ni 8f x = 0.1194, y = 0.231, z = 0.083
(room temp) b = 6.403 Mg1 8f x = 0.265, y = 0.483, z = 0.075
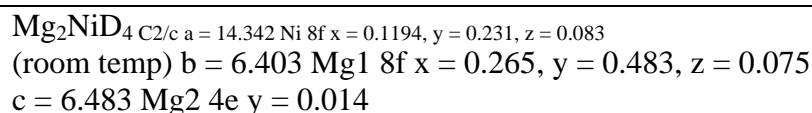c = 6.483 Mg2 4e y = 0.014

Table 1. Crystal structures of selected examples of binary alloys and ternary hydrides

The major difference between the hydrogen sites of binary and ternary hydrides is the kind of atoms surrounding the interstices. Only one kind of atom forms the interstitial sites in binary hydrides, whereas the interstices are surrounded by various combinations of the component atoms in ternary hydrides.

Therefore, the site preference depends on the size and the nature of participating atoms. It has been found that hydrogen prefers to occupy sites which are surrounded by at least one atom of stable hydride-forming metals. For example, in $TiFeD_{1.9}$ hydrogen atoms occupy the sites $[Ti_4Fe_2]$ and $[Ti_2Fe_4]$. In Laves phase hydride such as $ZrMn_2$, hydrogen atoms tend to occupy the sites $[Zr_3Mn]$ and $[Zr_2Mn_2]$.

It suggests that hydrogen atoms occupy the sites surrounded by the large numbers of hydride forming elements. As already described, the actual crystal structure of metal hydrides is sometimes deformed from the original alloys. The hydrogen interstitial site is also deformed in many cases but precis refinement of the atomic coordinates of such sites is difficult because of the corresponding lower resolution and sample-derived low quality diffraction data.

A general rule for the hydrogen-hydrogen bond lengths has been found. The distances between the hydrogen atoms in ternary hydrides were found to be less than 2.1 Å. There are a few exceptions but the experiments in which shorter H-H bond lengths were found are not reliable because of the difficulties of structural refinements using neutron data.

The distance between metal and hydrogen atoms in the ternary hydride is generally described as the sum of the atomic radii of corresponding metals and hydrogen. The radii of hydrogen atoms are usually about 0.4 Å.

The M-H distances in the ternary hydrides are sometimes shorter than in the binary hydrides. The reason for this phenomenon is due to the partial occupation of the hydrogen sites, which is more often found in the ternary hydrides.

Westlake postulates two structural criteria regarding H sites in metal hydrides. The hole size for a hydrogen atom is larger than 0.4 Å in a radius and the minimum H-H distance is 2.1 Å.

This postulate is of purely geometric origin and does not involve the nature of the metal atoms. However, as Westlake reported for $LaNi_5D_6$, $LaNi_4AlD_{4.5}$, ZrV_2D_6, $ZrMn_2D_{2.75}$ etc., the agreement with observed hydrogen site occupancies is fairly good.

The effectiveness of this model is still under discussion because it cannot predict any phase transformations or high-pressure phase when much more hydrogen is involved than predicted on the basis of the Westlake model.

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Biographical Sketch

Etsuo AKIBA: born 7 February 1952, in Sapporo, Japan; has received B.Sc. Degree in inorganic chemistry from Saitama University, M.Sc. Degree and Ph.D Degrees in physical chemistry from the University of Tokyo; joined National Chemical Laboratory for Industry (Present: National Institute of Materials and Chemical Research) in 1979; served also as Professor, Utsunomiya University from 1997; has published some 110 scientific papers, 50 reviews and 15 books on metal hydride, crystal structural analysis using the Rietveld method and hydrogen related energy systems.