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論　文

トリチウム用ゲッター材の開発指針

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A Guiding Rule to Design Tritium Getters

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Abstract

Hydrogen getter materials, most of which are metals and alloys forming hydrides, are attractive for the establishment of safe handling techniques of a large amount of tritium for the research and development of thermonuclear fusion reactors. To develop materials suitable for tritium handling, it is indispensable to find some guiding rules to predict thermodynamic parameters determining the equilibrium pressure of tritium.

From this viewpoint, we searched for the relations between the observed heat of hydride formation and physicochemical properties of metals and alloys for over 300 different data in about 100 systems. We found an empirical equation consisting of the electronegativities of hydrogen and hydride formers. This equation could evaluate the heat of the hydride formation for not only metals but also alloys consisting of even three or more components with the standard deviation of about 4 kcal/mol(hydride). Although this equation is not quite accurate, especially for those having relatively small heat of hydride formation, it can be applied as a powerful guiding rule to design tritium getters with adequate thermodynamic parameters for tritium handling.

1. Introduction

A wide variety of hydride forming materials, which are mostly metals and alloys, has been developed for storage/transport of hydrogen energy in the last two decades.[1] In this application, those hydrides are expected to show the equilibrium pressure about one to several atmospheric pressure at room temperature and high hydrogen/metal ratios (H/M) in hydrides. On the other extreme cases, metals and alloys showing very low equilibrium pressure for hydrogen and other gases have been developed for applying them as bulk getter pumps to obtain clean vacuum.[2]

Those materials are also interesting and promising to establish safe handling techniques of a large amount of tritium for the research and development of thermonuclear fusion reactors.[3] The properties of them, however, will have to be refined more for this application on 1) ease in activation, 2) adequate equilibrium pressure, which should be as low as possible at room temperature and about one atmospheric pressure at moderately high temperatures, for example at 500°C, 3) resistivity against powdering, 4) inflammability with air exposure at operating temperatures, 5) adsorption and desorption rate, 6) selectivity to absorb a given gas species in gas mixtures, 7) isotope effects on the equilibrium pressure and absorption/desorption rate, and 8) durability of the above mentioned characteristics. If those properties will be improved, they will undoubtedly be quite useful for the tritium processing consisting of storage-supply-recovery, purification of tritium gas containing impurity gases, and waste handling such as tritium solidification. In addition, if those materials show large isotope effects, they will be also valid for enrichment-separation of tritium in isotope mixtures.

From the viewpoint of the applications to tritium processing, we have studied equilibrium properties such as heat of hydrogen absorption as well as kinetics and mechanisms of the activation and absorption/desorption rate of three hydrogen isotopes using Zr-alloys as a model system.[4-12] We have found that the mechanisms are independent of the choice of alloying elements and alloy compositions. The equilibrium and kinetic parameters, however, are considerably dependent on the alloy systems.

To develop a getter suitable for a given unit process of the tritium processing, equilibrium properties such as heat of hydrogen absorption and/or hydride formation are of primary importance. Therefore, we have to develop some materials having suitable equilibrium parameters. For this purpose, some guiding rules are necessary. One of such rules is known as the rule of the reverse stability.[13,14] This is, however, applicable, as it stands, only to binary alloy systems, and even for them the estimated

heat does not necessarily agree well with the observed value. Another one is the nearest neighbor model.[15-17] To estimate the heat of hydride formation with this model, however, it is required to know the crystallographic and electronic structure as well as the interaction energy between host and hydrogen atoms. Namely, it will be applicable only to limited systems for which the above mentioned parameters are known.

On the other hand, in the course of our investigation for Zr-alloys we have observed a trend that the heat of hydrogen absorption increases with the decrease in the electronegativity of alloying element. Based on this observation, the present paper will describe an empirical relation between the electronegativities of materials and heat of hydride formation and/or of hydrogen absorption for various metals and alloys.

2. Assumptions to evaluate the electronegativities of alloys

The concept of electronegativity has been proposed by Pauling to explain bond strength of molecules and/or compounds.[18] This concept has been also successful in the field of solid state chemistry: namely, the heat of oxide formation for various metals is found to be linear functions of the electronegativities of metals.[19] Similar relations have been observed for the formation of hydroxide, sulfide, sulfate, nitrate and so on.[20] Those facts suggest that there will be similar relations between the heat of hydride formation and electronegativity of hydride former.

The electronegativities of elements have been reported by several authors. In the present paper, we used the values by Pauling cited from Huheey.[21] As for alloys, we adopted a similar assumption by Clifford,[22] who assumed the electronegativity of the OH radical to be $\chi_H/2+\chi_O/2=2.8$ to explain the change in the heat of hydroxide formation with various elements. We further extended this idea to alloys with even three or more components. For example, the electronegativity of an alloy, $A_xB_yC_z$ where A, B and C are the constituents of the alloy, and x, y and z are their atomic fraction, the electronegativity was assumed to be the weighted arithmetic mean: namely,

$$\chi(A_xB_yC_z)=x\chi_A+y\chi_B+z\chi_C \qquad (1)$$

where χ_A, χ_B and χ_C are the electronegativities of the constituents, A, B and C, respectively. It means that the alloy is assumed as if an element having the electronegativity of $\chi(A_xB_yC_z)$

3. Results and Discussion

3.1. Calculation of heat of hydride formation

According to Pauling, the enthalpy change for the formation of AB from AA and BB molecules is described as $Q=23(\chi_A-\chi_B)^2$ in kcal/mol unit. In the case of hydride formation described as $M+(s/2)H_2=MH_s$ where M is the hydride forming material and s is the stoichiometric number of hydrogen, the heat of hydride formation would be

$$(-\Delta H_f^\circ)=23s(\chi_M-2.20)^2 \qquad (2)$$

where χ_M and 2.20 are the electronegativities of the material and hydrogen, respectively. The values calculated from this equation, however, do not agree well with the observed ones. This is due to the fact that the hydride actually formed is not MH_s molecules.

On analogy from oxide formation,[22] we considered that some correlations would appear between the observed heat and the value calculated from Eq. (2). To look for such relations, over 300 data for metals and alloys in about 100 systems were cited from literature.[1,23,24] The data for alloys are mostly for so called hydrogen storage materials. Those data were compared with the values calculated from Eq. (2) and they were fitted with the least square method. Consequently, we found the following equation which reproduced fairly well the observed heat of hydride formation. It will be denoted as the calculated heat of hydride formation in the present study.

$$(-\Delta H)\mathrm{calc}=23s(\chi_M-2.20)^2+3.72s-3.72 \qquad (3)$$

The unit of the calculated heat is kcal/mol(hydride).

During the least square fitting, we observed that the heat of formation for trihydrides largely deviated from the calculated one. For those trihydrides, we took account of the fact that they have the first plateau in a region forming dihydride, and subsequently the second plateau appears in the trihydride phase. Therefore, it is considered that the formation of trihydride takes place in two step reactions as

$$M+H_2=MH_2 \qquad (4)$$

$$MH_2+(1/2)H_2=MH_3 \qquad (5)$$

It means that the heat of trihydride formation should be the sum of the heat for reactions (4) and (5). To calculate the heat for reaction (5), we assumed the

electronegativity of dihydride as

$$\chi(MH_2) = \chi_M/3 + 2\chi_H/3 \quad (6)$$

By using this value, the heat for reaction (5) could be evaluated from Eq. (3). This value was added to the heat of formation for reaction (4), which had been calculated from Eq. (3) and the sum was adopted as the heat of trihydride formation. This sum corresponds to the experimentally observed one.

With respect to Zr-alloys, we had to assume the stoichiometric number, s, because of the lack of experimental data. It was assumed that each of the constituents of a given Zr-alloy reacts stoichiometrically with hydrogen. For example, $ZrV_2+2H=ZrV_2H_4$, where the number 4 was evaluated as (ZrH_2+2VH). Similarly, we assumed Zr_2FeH_5 for $Zr_2Fe(2ZrH_2+FeH)$, Zr_2NiH_5 for $Zr_2Ni(2ZrH_2+NiH)$, $Zr_3Al_2H_8$ for

Table 1. Comparison of the two different calculations and observations for heat of hydride formation.

Material	$-\Delta H_{obs}$	$-\Delta H_{calc}$	
		Reference 14	Present study
$ScH_{1.86}$	45.1	43.0	33.4
TiH_2	30.4	31.8	23.7
$VH_{0.5}$	3.9	4.3	1.9
VH_2	13.0	8.0	18.6
CrH	1.9	1.4	6.7
$MnH_{0.8}$	0.9	4.8	7.3
$CoH_{0.5}$	0.0	1.1	-0.6
$NiH_{0.5}$	0.4	-1.4	-0.9
$YH_{1.8}$	47.7	41.8	42.2
$YH_{2.6}$	58.8	49.4	63.3
$ZrH_{1.4}$	29.7	37.3	25.8
ZrH_2	39.8	45.6	38.5
$NbH_{0.5}$	5.0	6.8	2.3
NbH_2	14.5	20.3	20.2
MoH	1.4	0.5	-0.1
$RhH_{0.5}$	-2.1	-1.4	-1.8
$PdH_{0.5}$	2.5	-0.7	-1.9
$LaH_{1.8}$	44.4	37.1	53.0
$LaH_{2.7}$	54.8	45.1	55.8
$HfH_{0.5}$	7.6	11.9	7.9
$HfH_{1.7}$	27.1	35.5	34.2
$TaH_{0.5}$	4.6	6.1	3.8
ThH_2	35.4	47.0	40.9
$ThH_{3.3}$	48.8	55.0	44.7
UH_3	30.5	17.2	24.6
PuH_2	37.6	26.0	40.9

$-\Delta H_{obs}$ and $-\Delta H_{calc}$ are in the unit of kcal/mol(hydride)

Zr_3Al_2 ($3ZrH_2+2AlH$) and so on. This assumption is quite similar to that adopted in the rule of reverse stability.[13]

3.2. Comparison of the calculated heat with observed one

A method to estimate the heat of hydride formation has been reported by Miedema *et al.*[13,14] To examine the validity of the present empirical equation, the values estimated from those two methods are compared with the observed ones. Table 1 summarizes the comparison of those three values for various hydrides and they are plotted in Fig. 1. In these table and figure, it is seen that the estimation by Miedema and Bouten[14] gives better agreement with the observed heat for some of hydrides than the present estimation, while the present one is better than the Miedema and Bouten's

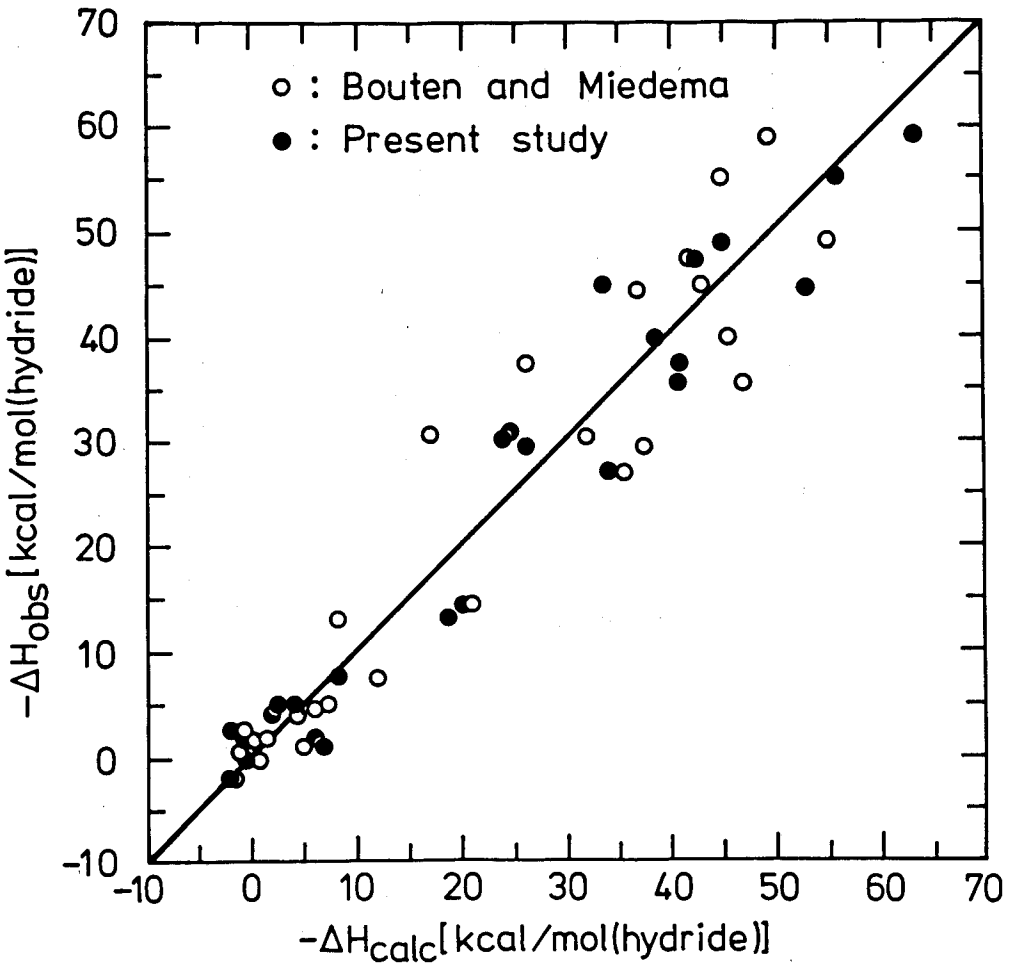

Fig. 1. Comparison of the observed heat of hydride formation for some metals and heat calculated with two different methods

Table 2. Summary of the observations and calculations with Eq. (3) for heat of hydride formation for various metals and alloys

Material	$-\Delta H_{obs}$[1*]	s	χ_M	$-\Delta H_{ob}$[2*]	$-\Delta H_{cal}$[2*]	Δ[3*]	Ref
ScH_2	41.40	2.00	1.36	41.40	36.14	5.26	1
$ScH_{(2-x)}$	48.00	2.00	1.36	48.00	36.14	11.86	1
$TiH_{1.1971}$	29.90	1.97	1.54	29.47	23.32	6.15	1
$TiH_{1.185}$	33.50	1.85	1.54	30.99	21.66	9.33	1
TiH_2	31.80	2.00	1.54	31.80	23.72	8.08	1
$VH_{0.5}$	8.28	0.50	1.63	2.07	1.87	0.20	1
YH_2	54.00	2.00	1.22	54.00	47.86	6.14	23
YH_2	44.40	2.00	1.22	44.40	47.86	- 3.46	1
YH_2	54.30	2.00	1.22	54.30	47.86	6.44	1
$ZrH_{1.5}$	30.00	1.50	1.33	22.50	27.94	- 5.44	1
$ZrH_{2.0}$	39.00	2.00	1.33	39.00	38.50	0.50	1
$NbH_{0.5}$	11.30	0.50	1.60	2.83	2.27	0.56	1
$NbH_{0.5}$	9.58	0.50	1.60	2.40	2.27	0.13	1
$NbH_{0.5}$	9.76	0.50	1.60	2.44	2.27	0.17	1
$PdH_{0.5}$	6.80	0.50	2.20	1.70	-1.87	3.57	1
LaH_2	49.60	2.00	1.10	49.60	59.34	- 9.74	23
LaH_2	49.70	2.00	1.10	49.70	59.34	- 9.64	1
$CeH_{1.9}$	52.00	1.90	1.12	49.40	54.28	- 4.88	1
CeH_{2-x}	54.90	2.00	1.12	54.90	57.33	- 2.43	1
CeH_{2-x}	49.20	2.00	1.12	49.20	57.33	- 8.13	1
CeH_2	49.30	2.00	1.12	49.30	57.33	- 8.03	23
PrH_2	49.70	2.00	1.13	49.70	56.35	- 6.65	1
PrH_2	47.80	2.00	1.13	47.80	56.35	- 8.85	1
PrH_2	49.30	2.00	1.13	49.30	56.35	- 7.05	23
NdH_2	50.50	2.00	1.14	50.50	55.37	- 4.87	1
NdH_2	44.80	2.00	1.14	44.80	55.37	-10.57	1
SmH_2	48.20	2.00	1.17	48.20	52.48	- 4.28	23
SmH_2	53.30	2.00	1.17	53.30	52.48	0.82	1
GdH_2	46.90	2.00	1.20	46.90	49.68	- 2.78	1
TbH_2	50.90	2.00	1.21	50.90	48.76	2.14	23

Table 2. (continued)

Material	$-\Delta H_{obs}$[1*]	S	χ_M	$-\Delta H_{ob}$[2*]	$-\Delta H_{cal}$[2*]	Δ[3*]	Ref
DyH_2	52.70	2.00	1.22	52.70	47.86	4.84	23
HoH_2	54.00	2.00	1.23	54.00	46.96	7.04	23
ErH_2	53.50	2.00	1.24	53.50	46.07	7.43	23
ErH_2	54.20	2.00	1.24	54.20	46.07	8.13	1
TmH_2	53.80	2.00	1.25	53.80	45.20	8.60	23
YbH_2	43.40	2.00	1.26	43.40	44.33	-0.93	23
LuH_2	49.50	2.00	1.27	49.50	43.47	6.03	23
$TaH_{1.5}$	8.60	0.50	1.50	2.15	3.77	-1.62	1
ThH_2	35.20	2.00	1.30	35.20	40.94	-5.74	1
ThH_2	34.30	2.00	1.30	34.30	40.94	-6.64	1
ThH_2	35.00	2.00	1.30	35.00	40.94	-5.94	1
UH_3	20.60	3.00	1.70	30.90	24.63	6.27	1
UH_3	19.20	3.00	1.70	28.80	24.63	4.17	1
UH_3	20.30	3.00	1.70	30.45	24.63	5.82	1
UH_3	20.50	3.00	1.70	30.75	24.63	6.12	1
UH_3	20.10	3.00	1.70	30.15	24.63	5.52	1
NpH_2	28.00	2.00	1.30	28.00	40.94	-12.94	1
PuH_2	37.40	2.00	1.30	37.40	40.94	-3.54	1
PuH_2	37.30	2.00	1.30	37.30	40.94	-3.64	1
PuH_2	35.40	2.00	1.30	35.40	40.94	-5.54	1
TiFeH	6.60	0.50	1.69	1.65	1.18	0.47	24
$TiFeH_{1.9}$	5.50	0.95	1.69	2.61	5.59	-2.98	24
$TiCoH_{1.4}$	13.80	0.70	1.71	4.83	2.74	2.09	24
$TiLaH_{1.4}$	13.80	0.70	1.71	4.83	2.74	2.09	24
$TiMn_{1.5}H_{2.47}$	6.80	0.99	1.55	3.36	9.66	-6.30	24
$ZrCoH_{1.8}$	16.40	0.80	1.61	6.56	5.77	0.79	27
$ZrCoH_{1.3}$	19.50	0.65	1.61	6.34	3.99	2.35	26
$LaNi_5H_6$	7.10	1.00	1.78	3.55	4.13	-0.58	24
$LaNi_5H_6$	7.20	1.00	1.78	3.60	4.13	-0.53	28
LaNi2H_2	12.40	0.67	1.64	4.14	3.56	0.58	28
$LaNiH_{3.9}$	25.00	1.95	1.51	24.38	25.16	-0.78	28

Table 2. (continued)

Material	$-\Delta H_{obs}$[1*]	s	χ_M	$-\Delta H_{ob}$[2*]	$-\Delta H_{cal}$[2*]	Δ[3*]	Ref
$La_7Ni_3H_{19}$	36.40	1.90	1.34	34.58	35.41	-0.83	28
$LaFe_5H_6$	19.00	1.00	1.71	9.50	5.55	3.95	24
$LaCr_5H_6$	25.00	1.00	1.57	12.50	9.20	3.30	24
$CeNi_5H_6$	3.40	1.00	1.78	1.70	4.08	-2.38	24
$PrNi_5H_6$	7.30	1.00	1.78	3.65	4.04	-0.39	24
$NdNi_5H_6$	7.00	1.00	1.78	3.50	4.00	-0.50	24
$MmNi_5H_{6.3}$	6.30	1.05	1.78	3.31	4.53	-1.22	24
$MmCo_5H_3$	9.60	0.50	1.75	2.40	0.46	1.94	24
$Ti_{0.9}La_{0.1}CoH_{1.3}$	13.20	0.75	1.69	4.95	3.58	1.37	24
$Ti_{0.9}V0_{0.1}COH_{1.4}$	15.90	0.70	1.72	5.57	2.66	2.91	24
$TiCo_{0.5}Mn_{0.5}H_{1.4}$	11.20	0.85	1.63	4.76	5.82	-1.06	24
$TiCo_{0.5}Fe_{0.5}H_{1.2}$	10.10	0.60	1.70	3.03	1.98	1.05	24
$TiCo_{0.75}Cr_{0.25}H_{1.3}$	12.10	0.65	1.71	3.93	2.22	1.72	24
$TiCo_{0.75}Ni_{0.25}H_{1.5}$	15.20	0.75	1.71	5.70	3.13	2.57	24
$TiFe_{0.5}Ni_{0.15}V_{0.05}H_{1.6}$	10.80	0.80	1.69	4.32	4.10	0.22	24
$Ti_{0.8}Zr_{0.2}Mn_{1.8}Mo_{0.2}H_3$	7.00	1.00	1.57	3.50	9.02	-5.52	24
$TiFe_{0.9}Cr_{0.1}H$	7.20	0.50	1.68	1.80	1.28	0.52	24
$TiFe_{0.8}Cr_{0.2}H$	8.50	0.50	1.67	2.13	1.38	0.74	24
$TiFe_{0.95}Mn_{0.05}H$	7.00	0.50	1.68	1.75	1.26	0.49	24
$TiFe_{0.9}Mn_{0.1}H$	6.60	0.50	1.67	1.65	1.35	0.30	24
$TiFe_{0.8}Mn_{0.2}H$	7.60	0.50	1.66	1.90	1.52	0.38	24
$TiFe_{0.9}Co_{0.1}H$	7.30	0.50	1.69	1.83	1.14	0.68	24
$TiFe_{0.9}Co_{0.2}H$	7.80	0.50	1.69	1.95	1.12	0.83	24
$TiFe_{0.9}Ni_{0.1}H$	8.30	0.50	1.69	2.08	1.13	0.94	24
$TiFe_{0.85}Ni_{0.15}H$	9.00	0.50	1.69	2.25	1.11	1.14	24
$TiFe_{0.8}Ni_{0.2}H$	10.00	0.50	1.69	2.50	1.09	1.41	24
$TiFe_{0.5}Ni_{0.5}H$	10.80	0.50	1.71	2.70	0.95	1.75	24
$La_{0.8}Nd_{0.2}Ni_5H_6$	7.20	1.00	1.78	3.60	4.11	-0.51	24
$La_{0.8}Gd_{0.2}Ni_5H_{4.5}$	7.20	0.75	1.78	2.70	2.13	0.57	24
$La_{0.8}Y_{0.2}Ni_5H_4$	7.20	0.67	1.78	2.40	1.47	0.93	24
$LaNi_4CuH_5$	9.60	0.83	1.77	4.00	2.86	1.14	24

Table 2. (continued)

Material	$-\Delta H_{obs}$[1*]	s	χ_M	$-\Delta H_{ob}$[2*]	$-\Delta H_{cal}$[2*]	Δ[3*]	Ref
$LaNi_{4.6}Al_{0.4}H_5$	8.70	0.83	1.76	3.62	3.16	0.47	24
$LaNi_{4.6}Mn_{0.4}H_5$	8.60	0.83	1.75	3.58	3.22	0.36	24
$LaNi_{4.6}Mn_{0.4}H_6$	8.60	1.00	1.75	4.30	4.62	-0.32	24
$LaNi_{4.6}In_{0.4}H_5$	9.50	0.83	1.77	3.96	2.97	0.99	24
$LaNi_{4.6}In_{0.4}H_6$	9.50	1.00	1.77	4.75	4.31	0.44	24
$LaNi_{4.6}Sn_{0.4}H_5$	9.20	0.83	1.77	3.83	2.94	0.89	24
$LaNi_{4.6}Sn_{0.4}H_6$	9.20	1.00	1.77	4.60	4.27	0.33	24
$LaNi_{4.6}Ga_{0.4}H_5$	8.40	0.83	1.77	3.50	2.94	0.56	24
$LaNi_{4.6}Ga_{0.4}H_6$	8.40	1.00	1.77	4.20	4.27	-0.07	24
$LaNi_{4.6}Si_{0.4}H_{3.5}$	8.50	0.58	1.77	2.48	0.87	1.61	24
$LaNi_{4.6}Ge_{0.4}H_4$	8.20	0.67	1.78	2.73	1.43	1.31	24
$Mm_{0.5}Ca_{0.5}Ni_5H_5$	7.60	0.83	1.77	3.17	2.95	0.21	24
$Mm_{0.9}Ti_{0.1}Ni_5H_{4.5}$	7.40	0.75	1.78	2.78	2.07	0.71	24
$MmNi_{4.5}Mo_{0.5}H_{6.6}$	4.20	1.10	1.80	2.31	4.48	-2.17	24
$MmNi_{4.5}Cr_{0.5}H_{6.3}$	6.10	1.05	1.76	3.20	4.88	-1.68	24
$MmNi_{4.5}Si_{0.5}H_{3.8}$	6.60	0.63	1.77	2.09	1.26	0.82	24
$MmNi_{4.5}Cr_{0.25}Mn_{0.25}H_{6.9}$	7.10	1.15	1.75	4.08	5.89	-1.81	24
$MmNi_{4.5}Mn_{0.45}Zr_{0.05}H_{5.2}$	7.90	0.87	1.74	3.42	3.65	-0.23	24
$MmNi_{4.5}Al_{0.5}H_{4.9}$	5.50	0.82	1.75	2.25	3.11	-0.86	24
$MmNi_{2.5}Co_{2.5}H_{5.2}$	8.40	0.87	1.76	3.64	3.30	0.35	24
$Mm_{0.75}Ti_{0.25}Ni_5H_{4.4}$	7.20	0.73	1.79	2.64	1.78	0.85	24
$Mm_{0.9}Ca_{0.1}Ni_5H_5$	6.60	0.83	1.77	2.75	2.86	-0.11	24
$Mm_{0.75}Ca_{0.25}Ni_5H_4$	7.80	0.83	1.77	3.25	2.89	0.36	24
$Mm_{0.5}Ca_{0.5}Ni_5H_5$	7.60	0.83	1.77	3.17	2.95	0.21	24
$Mm_{0.25}Ca_{0.75}Ni_5H_5$	7.10	0.83	1.76	2.96	3.02	-0.06	24
$MmNi_{4.5}Cr_{0.46}Mn_{0.04}H_{6.3}$	6.70	1.05	1.75	3.51	4.97	-1.46	24
$MmNi_{4.5}Mn_{0.05}H_{6.8}$	7.10	1.13	1.76	4.02	5.49	-1.47	24
$MmNi_{4.5}Mn_{0.5}Zr_{0.025}H_{5.9}$	9.70	0.98	1.74	4.75	4.60	0.14	24
$MmNi_{4.5}Mn_{0.5}Zr_{0.05}H_7$	7.90	1.16	1.74	4.57	6.14	-1.54	24
$MmNi_{4.5}Mn_{0.5}ZrH_{5.3}$	9.10	0.87	1.69	3.95	4.78	-0.82	24

Table 2. (continued)

Material	$-\Delta H_{obs}{}^{1*}$	s	χ_M	$-\Delta H_{ob}{}^{2*}$	$-\Delta H_{cal}{}^{2*}$	Δ^{3*}	Ref
$MmNi_{4.5}Mn_{0.475}Zr_{0.025}H_{6.2}$	6.10	1.03	1.74	3.15	5.04	-1.89	24
$MmNi_{4.5}Mn_{0.45}Zr_{0.1}H_{5.7}$	7.40	0.95	1.74	3.52	4.40	-0.88	24
$MmNi_{4.5}Al_{0.45}Ti_{0.05}H_{5.3}$	7.30	0.83	1.75	3.04	3.26	-0.22	24
$MmNi_{4.7}Al_{1.3}Ti_{0.05}H_{5.6}$	6.10	0.96	1.74	2.93	4.58	-1.65	24
$MmNi_{4.5}Al_{0.4}Zr_{0.1}H_5$	6.90	0.83	1.75	2.87	3.33	-0.45	24
ZrV_2H_4	35.00	1.33	1.53	23.33	14.97	8.35	29
Zr_2FeH_5	28.00	1.67	1.50	23.34	21.40	1.94	29
Zr_2NiH_5	29.00	1.67	1.52	24.17	20.02	4.15	29
$Zr_3Al_2H_8$	32.00	1.44	1.60	25.60	23.34	2.26	29
$Zr_{33}V_{33}Fe_{33}$	11.50	1.33	1.60	7.66	12.36	-4.70	29
$Zr_{33}V_{40}Fe_{27}H_{133}$	13.50	1.33	1.59	8.98	12.77	-3.79	29
$Zr_{33}V_{57}Fe_{10}H_{133}$	30.00	1.33	1.55	19.95	14.09	5.86	29
$Zr_{57}V_{36}Fe_7H_{156}$	28.00	1.57	1.44	21.98	23.11	-1.13	29

1 * : in kcal/mol(H_2) unit
2 * : in kcal/mol(Hydride) unit
3 * : $\Delta = (-\Delta H_{ob}{}^{2*}) - (-\Delta H_{cal}{}^{2*})$

for other hydrides. As a whole, the agreement between the observed and calculated heat is comparable for those two different estimation methods.

It should be mentioned here that the method by Miedema and Bouten requires the effective work functions, cell electron densities and molar volumes of host material and hydrogen.[14] They are, however, not always available, especially for multicomponent alloys. In fact, their method is not applicable for those alloys whose number of components is over three, as it stands, because of the lack of data mentioned above and/or methods to estimate them. On the contrary, the present method only needs to assume the additivity of electronegativities of constituents. In addition, the electronegativities of most elements have been determined and tabulated in the literature.[21] Consequently, it can be applied quite easily to the alloys of three or more constituents.

In Table 2 , the calculated values of heat of hydride formation are compared with the observed ones for various metals and alloys of over 300 data. It is seen in the table that the standard deviation of the calculated values from the observed ones is about 4 kcal/mol(hydride). They are plotted in Fig. 2 in double logarithmic scale. Some of

them which are attractive from the viewpoint of tritium handling are plotted in Fig.3 in enlarged scale for convenience. A fairly good linear relation is seen between the calculated and observed values in those figures, although there are some largely deviated points. In addition, in comparison with the relations observed for the enthalpy changes in the formation of oxide, hydroxide and others,[20] the scattering of the points in the present paper is somewhat larger. This is because the enthalpy changes for those reactions are much greater than that for hydride formation and hence small deviations disappear in the large values for those reactions. The scattering observed in the present study also arises from the fact that the present empirical relation does not take account of the electronic and crystallographic structures of host materials and resultant hydrides which undoubtedly play important roles for determining the heat of

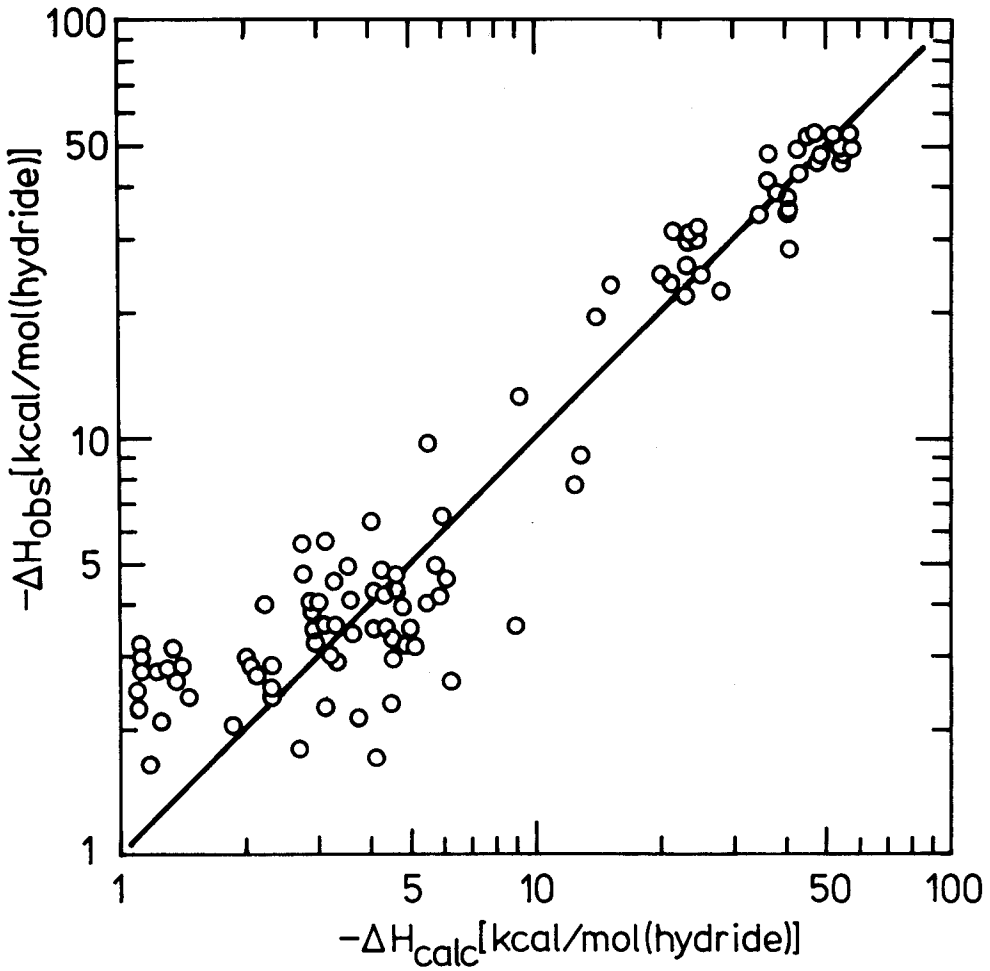

Fig. 2. Double logarithmic plots of the observed heat of hydride formation against calculated one from Eq. (3)

hydride formation. It should be mentioned here that the present empirical equation is not valid for alkali and alkaline earth metals. The calculated values using Eq. (3) for them are largely deviated from the observed ones. That is, the present equation is not applicable for the ionic hydrides.

In spite of the fact that the electronegativity concept has been originally proposed to explain the stabilization of the bond of a heteronuclear molecule by resonance, it is apparent that this concept is quite valid to estimate enthalpy changes for a wide variety of solid state reactions including the formation of oxide, hydroxide, sulfide, nitride and hydride, although some correction factors are added to the term of 23s $(\chi_M - \chi_g)^2$ for those solid state reactions.[20] With respect to those correction terms, the requirement for them is considered to arise from the fact that a solid material is not an aggregation of isolated molecules, but it is a material having definite crystallographic and electronic structure.

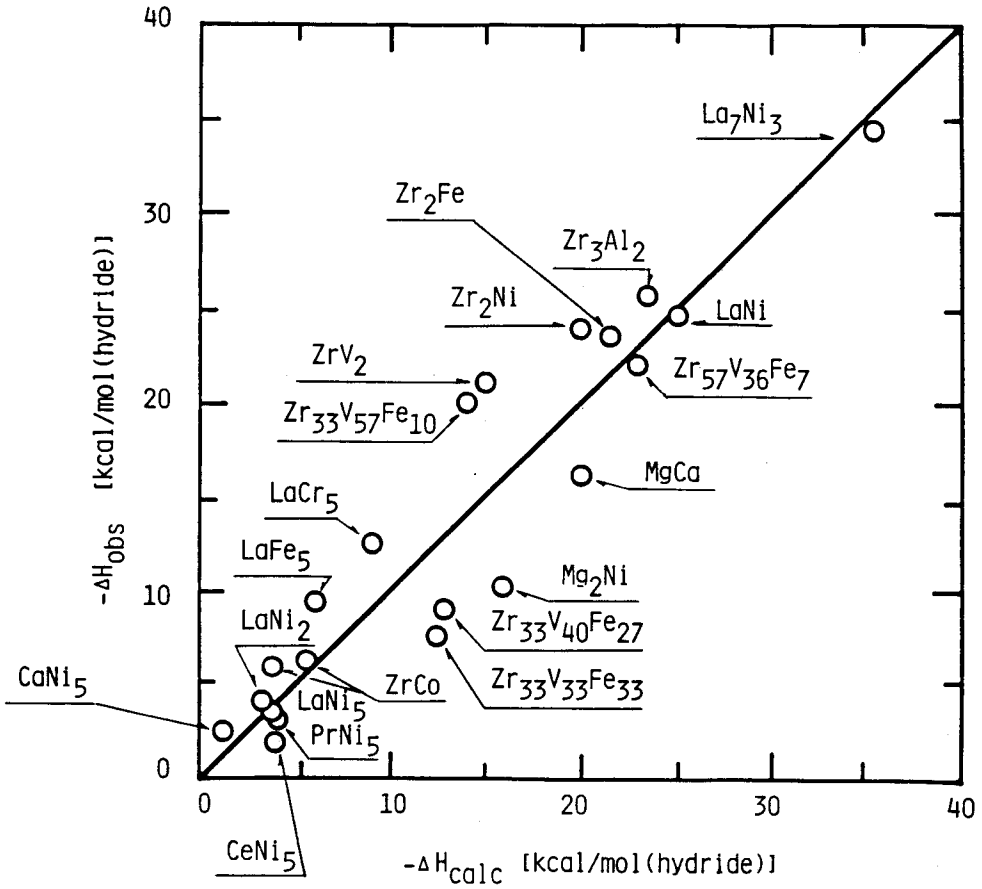

Fig. 3. Comparison of the observed heat and calculated one for some alloys which are attractive to tritium handling

The presence of the close correlation between the observed heat of hydride formation and the electronegativity indicates that the resonance stabilization of bonds is of prime importance. This is especially true for the hydrides showing large enthalpy change because the contribution of the correction terms is much smaller than that of the first term in Eq. (3). This means that the nearest neighbor interaction plays a dominant role to determine the heat of hydride formation. On the other hand, the difference in the crystallographic and electronic structures of solid materials appears to play a minor role. This is partly due to the fact that the value of electronegativity of a given element is an average over a number of different chemical bonds and/or materials containing the element and hence the effects of the crystallographic and electronic structure may be buried in the averaged value. This is a reason that the structure effect appears to be minor. It should be mentioned here, however, that the electronegativity of an element changes with the hybridization of electron orbits which participates the formation of a chemical bond. [21,25] Consequently, it changes with crystallographic and electronic structures. This appears to be also a reason of the scattering of the points in the figures of the present paper.

4. Conclusions

An empirical equation was presented to estimate the heat of hydride formation and/or hydrogen absorption. This equation contains only the electronegativity of element and the stoichiometric number of hydrogen in hydride. To apply this equation for alloys, it requires only a simple assumption that the electronegativity of the alloy is the weighted average of the electronegativities of the constituents. Because the electronegativities of most elements have been determined and tabulated in the literature, it can be applied quite easily to alloys consisting of even three of more components as well as metals. Consequently, the present method is more advantageous in comparison with Miedema and Bouten's method and/or the nearest neighbor model, although there are several defects in the present relation: namely, 1) dearth of sufficient accuracy, 2) ambiguity of theoretical significance, 3) want of a-priori determination of the stoichiometric number, s, and 4) inapplicability to alkali and alkaline earth metals. They are , however, surpassed with the advantages mentioned above. It can be, therefore, applied as a powerful guiding rule to develop not only hydrogen storage materials, but also tritium getters for the safe handling of a large amount of tritium consisting of storage, supply, recovery and so on.

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References

1) for example, W.M.Mueller, J.P.Blackledge and G.G.Libowitz, "Metal Hydrides", (Academic Press, 1968)

2) for example, P.A.Redhead, J.P.Hobson and E.V.Kornelsen, "The Physical Basis of Ultrahigh Vacuum", (Chapman and Hall, 1968)

3) for example, "Handling of Tritium-Bearing Wastes", (Intern. Atomic Energy Agency, 1981)

4) N.Inoue, K.Ichimura, K.Watanabe and T.Takeuchi, Ann. Rept. Tritium Res. Centr., **3** (1983) 33.

5) K.Ichimura, N.Inoue, K.Watanabe and T.Takeuchi, J. Vac. Sci. Technol., **A2** (1984) 1341.

6) K.Ichimura, N.Inoue, K.Ashida, K.Watanabe and T.Takeuchi, J. Nucl. Mater., **128/129** (1984) 876.

7) K.Ichimura, K.Ashida, M.Matsuyama, K.Watanabe and T.Takeuchi, Ann. Rept. Tritium Res. Centr., **4** (1984) 126.

8) K.Ichimura, K.Ashida and K.Watanabe, J. Vac. Sci. Technol., **A3** (1985) 346.

9) K.Ichimura, M.Matsuyama, K.Watanabe and T.Takeuchi, Fusion Technol., **8** (1985) 2407.

10) K.Ichimura, M.Matsuyama and K.Watanabe, J. Vac. Soc. Jpn., **29** (1986) 369.

11) K.Ichimura, M.Matsuyama and K.Watanabe, J. Vac. Sci. Technol., **A5** (1987) 220.

12) K.Ichimura, M.Matsuyama, K.Watanabe and T.Takeuchi, ibid., **A6** (1988) 2541.

13) H.H. van Mal, K.H.Buschow and A.R.Miedema, J. Less-Common Metals, **35** (1974) 147.

14) P.C.Bouten and A.R.Miedema, ibid., **71** (1980) 147.

15) I.Jacob, D.Shaltiel, D.Davidov and I.Miloslavski, Solid State Commun., **23** (1977) 669.

16) I.Jacob and D.Shaltiel, J. Less-Common Metals, **65** (1979) 117.

17) M.H.Hinz, S.Vaknin, S.Biderman and Z.Hadari, J. Appl. Phys., **52** (1981) 463.

18) L.Pauling, "The Nature of the Chemical Bond", (Cornell Univ. Press, 1960)

19) L.Brewer, Chem. Rev., 52(1953) 1: K.Tanaka and K.Tamaru, J.Catalysis, **2** (1963) 366.

20) K.Tanaka, in "Catalyst Handbook (in Japanese)", ed. by A.Ozaki, K.Tamaru, K.Tanabe and S.Nishimura, (Chijinshokan, 1967)

21) J.E.Huyeey, "Inorganic Chemistry: Principles of Structure and Reactivity", (Harper & Row, 1983)

22) A.F.Clifford, J. Am. Chem. Soc., **79**(1957) 5404 : J. Phys. Chem ., **63**(1959) 1227.

23) G.G.Libowitz and A.J.Mealand, in "Handbook on the Physics and Chemistry of Rare Earths", ed. by K.A.Gschneider,Jr. and L.Eyring, (North-Holland Pub., 1979), p .299.

24) Y.Ohsumi, "Zohho Kinzoku Suisokabutsu - sono Bussei to Ohyou (in Japanese)", (Kagaku Kohgyou Sha, 1986)

25) R.McWeeny, "Coulson's Valence", (Oxford Univ. Press, 1979)

26) T.Nagasaki, S.Konishi, H.Katsumata and Y.Naruse, Fusion Technol., **9** (1986) 506.

27) E.Willin, M.Sirch, P.-D.Penzhorn and M.Devillers, Fusion Technol., **14**(1988) 756.

28) G.Busch, L.Schlapbach and Th. von Waldkirch, "Hydride for Energy Storage (Proc. Intern. symp., Geilo, Norway, 1979)", (Oxford Press, 1978) p .1978.

29) see references in 12)