論　文

Zr-Ni 合金による重水素の吸蔵・脱離と合金化効果

芦田　　完・渡辺　国昭

沢田　英一[*1]・多々　静夫[*1]・池野　　進[*2]

富山大学水素同位体機能研究センター
富山大学工学部物質工学科[*1]
富山大学地域共同研究センター[*2]
〒930 富山市五福3190

Absorption and Desorption Kinetics of Deuterium for ZrNi System

Kan ASHIDA, Kuniaki WATANABE
Eiichi SAWADA[*1], Sizuo TADA[*1]
and Susumu IKENO[*2]

Hydrogen Isotope Research Center,
Metarial Sci. and Eng., Faculty of Eng.[*1]
Center for Cooperative Research[*2]
Toyama University, Gofuku 3190, Toyama 930, Japan
(Received August 31, 1993 ; accepted November 7, 1993)

Abstract

Because of the limited nature of elemental metals, most of the hydrogen storage materials are used as alloys. To apply hydrogen storage materials to tritium processing systems, it is indispensable to understand alloying effects on their properties such as storage, supply, recovery, separation and others to develop/design new materials. From this viewpoint, alloying effects on the ab/desorption kinetics of deuterium for the Zr-Ni system was studied. It was revealed that the absorption of deuterium obeys first order kinetics with respect to the deuterium pressure, whereas, the desorption obeys second order kinetics with respect to the amount of deuterium absorption. In addition, alloying Zr with Ni caused an increase in the activation energy for absorption ; on the contrary, the activation energies for desorption decreased. The heat of the deuterium solution and/or deuteride formation, evaluated through the proposed potential energy diagram, was found to decrease with increasing Ni Content.

Kan Ashida, Kuniaki Watanabe, Eiichi Sawada, Sizuo Tada, Susumu Ikeno

1. Introduction

Some metals and alloys forming stable hydrides have potential for tritium processing in thermonuclear fusion devices such as storage[1-3], supply[4,5], recovery[6-10], separation[11] and others[12-16]. Various properties, however, are required depending on their applications, for example, low equilibrium pressure at around room temperature for storage, high equilibrium pressure at moderate temperature around 500℃ for supply, high ab/desorption rate for recovery/supply, and so on. To meet these requirements, most of the hydrogen storage materials are used as alloys because of the limited nature of elemental metals.

To develop/design new materials, it is indispensable to understand alloying effects on their physicochemical properties such as electronic[17] as well as crystallographic structure[18,19], and thermodynamic and kinetic properties against hydride formation and/or decomposition[7,13,14]. A number of theoretical[17] as well as experimental studies[2-16] have been carried out. However, the accumulation of experimental data is still a matter of importance in order to investigate in more detail the alloying effects.

From the viewpoint of the practical importance of the ab/desorption rates of tritium by/from hydrogen storage materials, the alloying effects on the absorption and desorption kinetics were studied using deuterium as an alternative of tritium for ZrNi alloys which were selected as a model system.

2. Experimental

2. 1. Sample and apparatus

Samples were selected from the intermetallic compounds of Zr and Ni. There are eight intermetallic compounds in the Zr-Ni system as shown in Fig. 1[19]. In this study, Zr_2Ni_1(cubic), Zr_1Ni_1(orthorhombic), Zr_9Ni_{11}(cubic) and Zr_8Ni_{21}(triclinic) were used, which were purchased from Japan Metals & Chemicals Co. These compounds were prepared with arc melting method. They were examined with x-ray diffraction spectroscopy to confirm their structures before use. The samples used in the ab/desorption measurements were granular about 0.5 mm in diameter. Deuterium gas was purchased from Nippon Sanso Co. being guaranteed as 99.9%, and used without further purification.

Figure 2 shows the schematic drawing of the high vacuum system used in the present study. The system was equipped with a B-A type ionization vacuum gauge (ANELVA, NI-10D), a capacitance manometer (MKS Baratron, 113A with 1000 Torr

head), and a quadru-
pole mass spectrometer
(ULVAC, MSQ-150A).
The system was evacu-
ated with a sputter ion
pump and a turbo-
molecular pump backed
with an oil-sealed rotary
pump. The residual pres-
sure of the system
was routinely below 2
$\times 10^{-6}$ Pa, with the
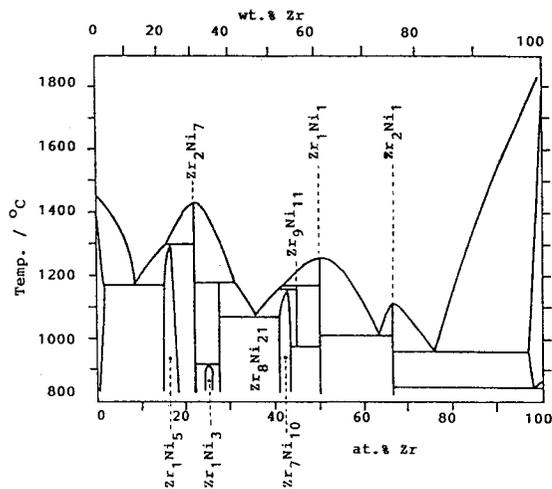main residual gases of
H_2, H_2O and CO.
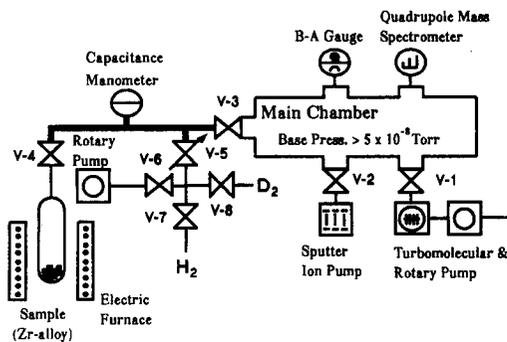

Fig. 1   Phase diagram of Zr-Ni system.

Fig. 2   Schematic drawing of the apparatus used.

2. 2. Ab/desorption measurements

The amounts of samples used were in a range from 150 to 1550 mg, depending on their reactivities against deuterium. The sample was always activated by vacuum heating at 800℃ for 30 min before each run, and, then it was cooled to a given temperature. After the temperature being kept constant, deuterium gas was introduced into the closed part of the system enclosed by V-3, V-4, and V-5 valves. Subsequently, the V-4, valve opened quickly, and the time course of pressure decay due to the absorption was measured using the capacitance manometer. The kinetics of the absorption was analyzed through the decay curve of the deuterium pressure. The metal to deuterium

65

ratio in the present sutdy was in the range from $x = 0.1$ to 2.0 for $(Zr_aNi_b)D_x$.

After an absorption measurement, the sample was heated linearly with time from the temperature to 800℃ to desorb the absorbed deuterium. The heating rate of the sample in this study was varied from 7 to 17 K/min. The pressure of desorbing deuterium was measured with the mass spectrometer. The kinetics of the desorption was analyzed through mass analyzed thermal desorption spectrum (TDS) of deuterium.

3. Results and discussin

3. 1. Absorption process

The ratio of the number of surface atoms (denoted as S) to that of the bulk (denoted as B) for a spherical particle is given by

$$S/B = 3/(r/d) \tag{1}$$

where r and d represent radius of spherical particle and the atomic distance, respectively. If we assume that the granules of the samples are spheres of about 0.5 ㎜ in diameter, the S/B ratio was roughly estimated to be 3.6×10^{-6}, where $r = 0.25$ and $d = 3 \times 10^{-7}$ ㎜ are taken as plausible values. This result indicate that the ratio of the number of surface atoms to that of bulk does not exceed 3.6×10^{-6}. It is also valid that hydrogen to metal ratio does not exceed this value as far as deuterium adsorption on the sample surface is considered. On the other hand, the observed ratio was in the range from 0.1 to 1, being 4 or 5 order of magnitude greater than the above estimation. Namely, the observed pressure decay was due to absorption by the bulk of samples.

In general, the absorption rate of hydrogen isotopes would be expressed as

$$-(dQ/dt) = kP^n$$
$$= k_aP^n (k_a = k/V) \tag{2}$$

where P is the pressure of hydrogen isotopes, k the absorption rate constant, V the volume of the system, and n the order of reaction. For most of the Zr-based alloys, n is known to be unity[20,21]. In this case, equation (2) is rewritten as follows.

$$\ln[(P_n - P_0)/(P_{n-1} - P_0)] = k_a(t_{n-1} - t_n)$$
$$\ln(\Delta P_n/\Delta P_{n-1}) = k_a\Delta t_n \tag{3}$$

Equation (3) indicates that the plots of Δt_n vs. $\ln(\Delta P_n/\Delta P_{n-1})$ give a straight line when the absorption process obeys the first order kinetics. Figure 3 shows the plots

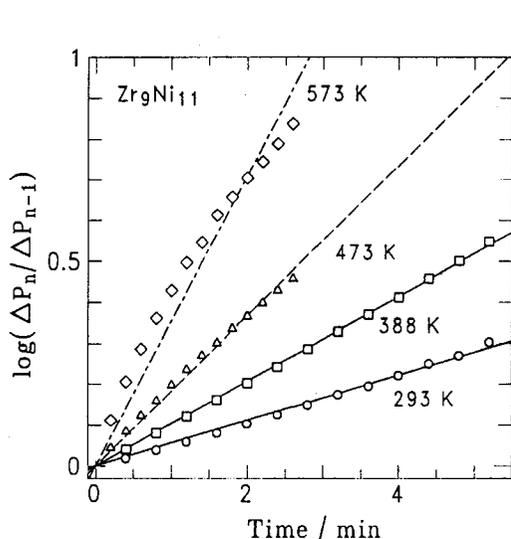Fig. 3   Plots of $\ln(\Delta P_n/\Delta P_{n-1})$
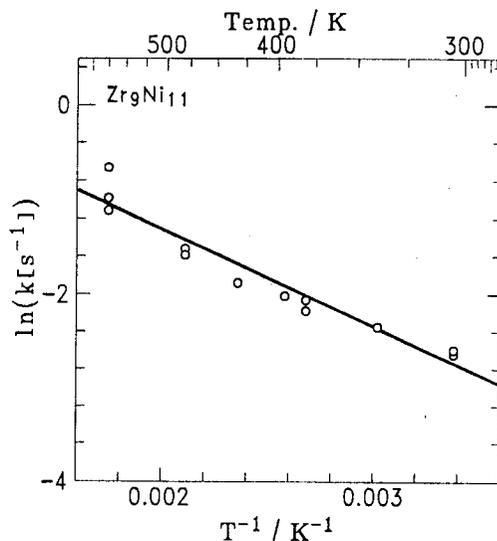against Δt_n for Zr_9Ni_{11}.

Fig. 4   Arrhenius plots of absorption
rate constants for Zr_9Ni_{11}.

of $\ln(\Delta P_n/\Delta P_{n-1})$ against Δt_n for Zr_9Ni_{11} at various temperatures. Each of the plots shows fairly well linearity, indicating that the absorption obeys the first order kinetics. Similar results were observed for other samples. The first order kinetics indicates that the rate determining step for absorption is the first order dissociation reaction of gaseous or adsorbed deuterium molecules on the surface, and the rate equation can be expressed for all of the samples used as follows.

$$-(dP/dT) = k_a P^{1.0} \tag{4}$$

$$k_a = \nu_a \exp(-E_a/RT) \tag{5}$$

where ν_a is the frequency factor for absorption and E_a the activation energy for absorption.

From the slope of each line in Fig. 3, the rate constant, k_a, for respective temperatures were evaluated for Zr_9Ni_{11}. Figure 4 shows the Arrhenius plots of the rate constant for the absorption of deuterium by Zr_9Ni_{11}. From the slope of the plots, the activation energy was evaluated to be 2.1 kcal/mol(D_2). The absorption kinetics and mechanism of deuterium were the same for other samples. The activation energies for other samples were also evaluated similarly as 1.0(Zr_2Ni_1), 1.6(Zr_1Ni_1) and 4.2($Zr_8 Ni_{21}$) kcal/mol(D_2). Figure 5 shows the plots of the activation energies against the alloy composition. From this figure, the activation energy for absorption was found to increase with increasing Ni content in the Zr-Ni system. The frequency factor for

absorption could be also evaluated from the intersection of the straight line with vertical axis in Arrhenius plot diagram (Fig. 4). In the present study, however, the frequency factor has not much physical significance, because the specific surface areas of the samples were not measured.
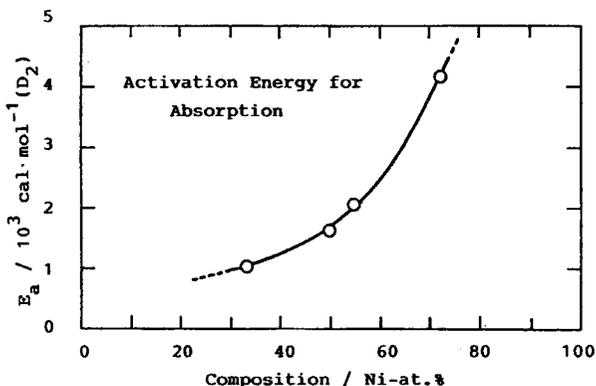

Fig. 5 Plots of activation energies for absorption against alloy composition for the Zr-Ni system.

3. 2. Desorption process

Figure 6 shows TDSs of deuterium for Zr_9Ni_{11}. Each of these spectra consisted of a single desorption peak and the peak shifted toward the lower temperature side with increasing amount of absorption. Similar peak shift has been observed for other samples.

As a first step, the possibility of diffusion limited desorption mechanism was examined. In this case, the desorption rate was given by the following equation, being assumed to the radial diffusion[22].
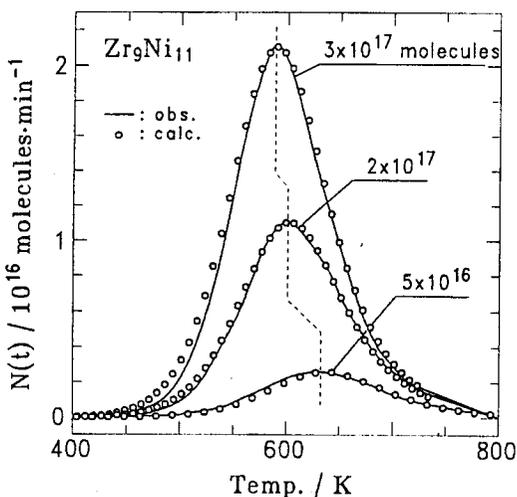

Fig. 6 TDSs of deuterium from Zr_9Ni_{11}. (dotted curves represent calculated spectra using $E_d = 19.0$ kcal/mol(D_2) and $\nu_d = 7.5 \times 10^{-12}$ molecules^{-1}s^{-1})

$$M(t) = \sigma_M [1 - (6/\pi^2) \sum_{n=1}^{\infty} (1/n^2) \exp(-Dn^2\pi^2 t/r^2)] \qquad (6)$$

where D is the diffusion coefficient, σ_M the total deuterium uptake, M(t) the desorbed deuterium at time t, and r the radius of the sphere particle. Examples of the calculated desorption spectra were shown in Fig. 7. In addition, the diffusion constant of hydrogen in Zr which was quoted from literature[23] was used for calculation because of
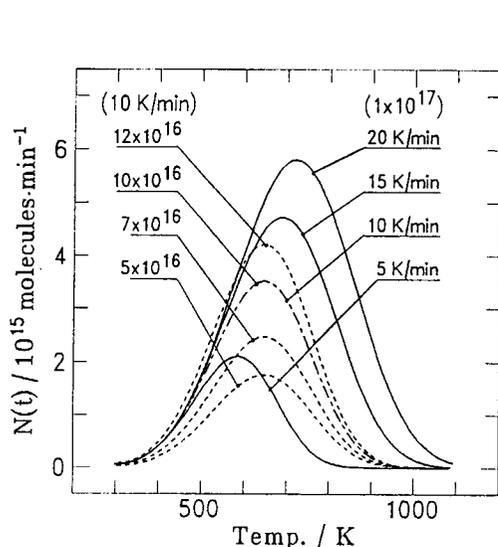
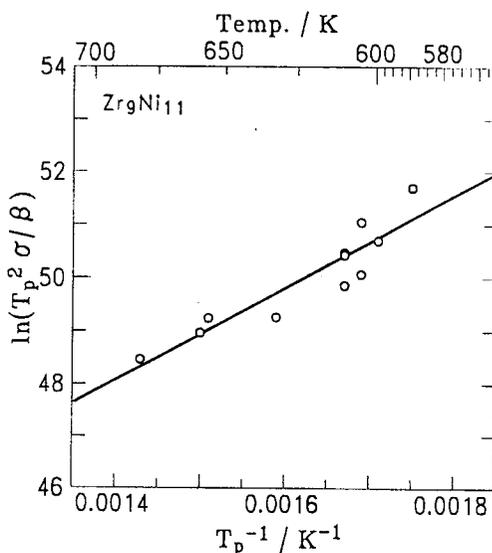Fig. 7   Calculated TDSs based on the diffusion limited mechanism assuming radial diffusion.

Fig. 8   Plots of $\ln(T_p{}^2/\beta)$ against $1/T_p$ for Zr_9Ni_{11}.

the lack of diffusion date of hydrogen isotopes in the Zr-Ni system. This figure shows that in the case of a diffusion limited desorption mechanism, there are typical differnces between calulated spectra and that of observed ones : namely, 1 : the desorption peak does not shift with increasing amount of absorption when the heating rate is kept constant, and 2 : the calculated desorption spectra shows rather wide FWHM (Full Width at Half Maximum) with factor of two or more in comparision with the observed ones.

As for the surface reaction mechanisms, the desorption rate would be expressed, in general, as follows.

$$N(t) = k_d \sigma^n \tag{7}$$

$$k_d = \nu_d \exp(-E_d/RT) \tag{8}$$

where σ is the amount of absorption, k_d the desorption rate constant, ν_d the frequency factor for desorption, and E_d the activation energy for desorption. Differentiating equation (7) with T by taking account of $T = T_0 + \beta t$ and taking $[dN(t)/dT] = 0$ at the peak temperature, T_p, one obtains the following equations.

$$(E_d/RT_p{}^2) = (n \nu_d \sigma^{n-1}/\beta) \exp(-E_d/RT_p) \tag{9}$$

case 1, n=1 :

$$\ln(T_p{}^2/\beta) = (E_d/RT_p) + \ln(E_d/R\nu_d) \tag{10}$$

69

case 2, n=2 :

$$\ln(T_p^2 \sigma / \beta) = (E_d/RT_p) + \ln(E_d/2R \nu_d) \tag{11}$$

Case 1 appears not to be plausible because Eq.(10) indicates that the desorption peak temperature, T_p, is independent of the amount of deuterium absorption, σ, being contradicted to the observations. On the other hand, the peak temperature and the amount of deuterium absorption depend each other in case 2. Equation (11) indicates that the plots of $\ln(T_p^2 \sigma / \beta)$ against T_p give a straight line when the desorption obeys the second order kinetics. Figure 8 shows an example of the plots for Zr_9Ni_{11}. A straight line could be drawn using the least square method. A unique set of the activation energy and the frequency factor for desorption could be evaluated from the slope of this line and the intersection with vertical axis as 19.0 kcal/mol(D_2) and 7.5×10^{-12} molecules^{-1}s^{-1}, respectively. The circles in Fig. 6 show calculated desorption spectra using these parameters. Agreement with the observed spectra indicates that the desorption process obeys the second order kinetics and the parameters, ν_d and E_d, are valid as well.

The activation energies for other samples were also evaluated from similar analysis as 27.0 (Zr_2Ni_1), 22.0 (Zr_1Ni_1) and 15.0 (Zr_8Ni_{21}) kcal/mol(D_2). Figure 9 shows the plots of activation energies against the alloy composition. This figure shows that the activation energy for desorption decreases with increasing Ni content in the Zr-
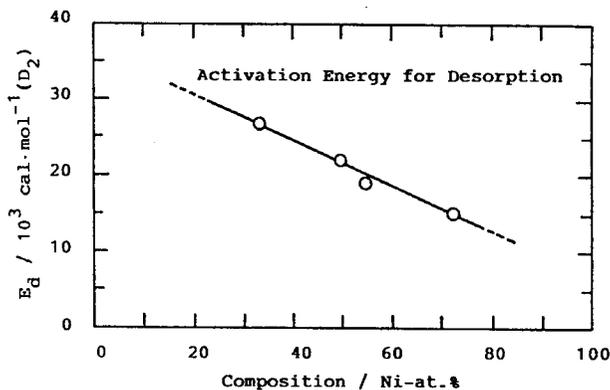

Fig. 9 Plots of activation energies for desorption against alloy composition for the Zr-Ni system.

Ni system. The observed frequency factors, however, could not compared each other because of the lack of data for specific surface areas.

3. 3. Alloying effects

The potential energy diagram for the absorption and desorption of deuterium in /from the Zr-Ni system should be drawn schematically as shown in Fig. 10[21]. From this diagram, the heat of deuterium solution and/or deuteride formation, ΔH, can be

approximated to the differ-
ence in the activation energy
between the absorption and
the desorption. Figure 11 shows
the plots of the heat of deu-
terium solution and/or deute-
ride formation observed in
the present study against alloy
composition with those by
others[7, 24], including the data
for deuteride formation by
Watanabe et al. This figure
indicates that $-\Delta H$ decrease
with increasing Ni content,
being agreed with a generally
observed trend that hydride
forming potential decreases
with alloying a hydride form-
ing element with a nonhydride
former. The hydride forming
potential is closely related to
the difference in the electro-
negativity between a metal
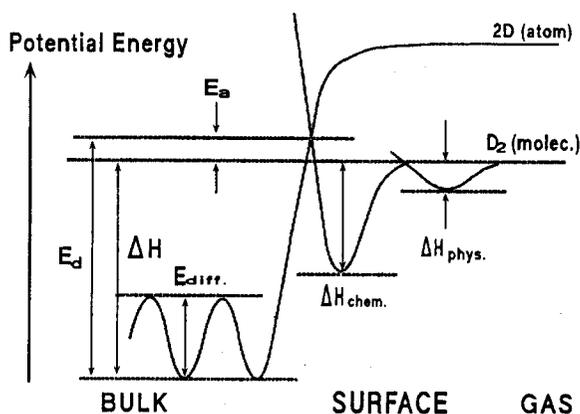(alloy) and hydrogen. These

Fig. 10 Schematic potential energy diagram for
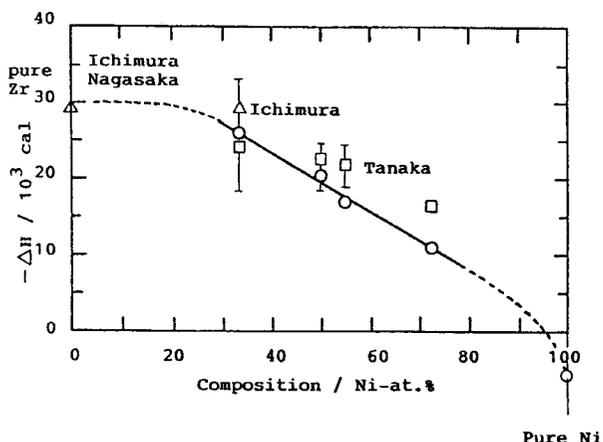the absorption and desorption of deuterium
for the Zr-Ni system.

Fig. 11 The heat of deuterium solution and/or
deuteride formation for ZrNi alloy composi-
tion

relation is expressed by the following empirical equation[25, 26].

$$(-\Delta H_{calc}) = 23s(\chi_M - 2.20)2 + 3.72(s-1) \qquad (12)$$

where s is the stoichiometric number of hydrogen in the hydride (MH$_s$, s＝2 in the
present study), and χ_M and 2.20 are the electronegativities of material M (metal or
alloy) and hydrogen, respectively. The values calculated from Eq.(12) are plotted against
observed ones in Fig.12. The fairly good agreement between them is observed in spite
of the difference in hydrogen content ፡ namely, experimental values obtained under
relatively low deuterium concentrations comparing with the stoichiometric number of
hydrogen, s, of the hydride equation (12). Nevertheless, Fig. 12 still suggests that elec-
tronic factors play an important role for hydrogen isotope solution and/or hydride

formation for the Zr-Ni system.

4. Conclusions

On account of the practical impor-
tance for the rates of tritium uptake
and/or release for hydrogen storage
materials, the present study is concern-
ed with the elucidation of alloying ef-
fect on ab/desorption kinetics of deute-
rium in/from the Zr-Ni system. Based
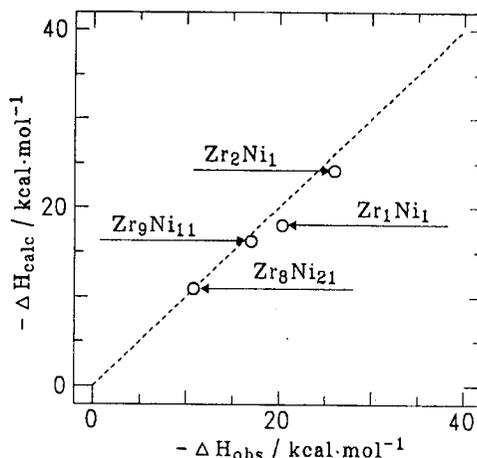on the above mentioned results and dis-
cussion, we conclude the followings :

Fig. 12 Comparison of $-\Delta H_{calc}$ and $-\Delta H_{obs}$ for deuterium solution and/or deuteride formation for the Zr-Ni system.

1. The absorption of deuterium obeys
   the first order kinetics with respect
   to the deuterium pressure, and the
   rate determining step for absorption is the dissociation of deuterium molecules on
   the sample surface.

2. The desorption of deuterium obeys the second order kinetics with respect to the
   amount of deuterium absorption, and the rate determining step for desorption is the
   association of deuterium atoms on the surface.

3. Alloying Zr with Ni caused to increase the activation energy for absorption ; on
   the contrary, the activation energy for desorption decreased. The heat of deuterium
   solution and/or deuteride formation was found to decrease with increasing Ni content.

4. The changes in ΔE_a, ΔE_d and $-\Delta H$ were smooth functions of the composition
   of the compounds : namely, there is no characteristic feature suggesting the impor-
   tance of the crystallographic structures. Consequently, the present results strongly
   suggest that electronic factors play important roles to determine the above mention-
   ed values.

References

1) E.H.P. Cordfunke, "The Chemistry of Uranium", Elsevier, Amsterdam, 1969.

2) T. Yamamoto, T. Yoneoka, S. Kokubo and M. Yamawaki, Fusion Eng. and Des., **7** (1989) 363.

3) R.-D. Penzhorn, M. Devillers and M. Sirch, J. Nucl. Mater., **170** (1990) 217.

4) K. Watanabe, K. Tanaka, M. Matsuyama and K. Hasegawa, Fusion Eng. and Des., **18** (1991) 27.

5) K. Ashida, M. Watanabe, C. Takeda, H. Anada, S. Ikeno and K. Watanabe, Ann. Rept. of Hydrogen Isotope Research Center, **10&11** (1991) 27.

6) C. Boffito, B. Ferrario. P. della Porta and L. Rosai, J. Vac. Sci. Technol., **18** (1981) 1117.

7) K. Ichimura, M. Matsuyama, K. Watanabe and T. Takeuchi, J. Vac. Sci. Technol., **A6** (1988) 2541.

8) H.F. Dylla, J.L. Cecchi and M. Ulrickson, J. Vac. Sci. Technol., **18** (1981) 1111.

9) R.J. Knize, J.L. Cecchi and H.F. Dylla, J. Vac. Sci. Technol., **20** (1982) 1135.

10) C. Boffito, B. Ferrario and D. Martelli, J. Vac. Sci. Technol., **A1** (1983) 1279.

11) K. Watanabe, K. Ashida, K. Ichimura and T. Takeuchi, Ann. Rept. of Tritium Res. Center, **8** (1988) 17. (in Japanese)

12) H. Albrecht, R.-D. Penzhorn, Th. Kastner and M. Sirch, Proc. Int. Symp. on Fusion Nucl. Technol., Tokyo, Japan, 1988, part, C, p.349.

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

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

15) K. Watanabe, M. Matsuyama, K. Ashida and H. Miyake, J. Vac. Sci. Technol., **A7** (1989) 2725.

16) N.J. Clark and E. Wu, J. Less-Com. Met., **163** (1990) 227.

17) For example, C.D. Gelatt, H. Ehrenreich and J.A. Weiss, Phys. Rev., **B17** (1979) 1940, P.C.P. Bouten and R. Miedema, J. Less-Com. Met., **71** (1980) 147, F.M. Mueller, A.J. Freeman, J.O. Dimmock and A.M. Furdyna, Phys. Rev. B, **1** (1976) 4617.

18) For example, A. Hellawell and W. Hume-Rothery, Phil. Mag., **45** (1954) 797, P. Nash and C.S. Jayanth, Bull. Alloy Phase Diagrams, **5** (1984) 144.

19) K. Bhanumurthy, B.B. Kale, S.K. Hhera and M.K. Asundi, Metallurgical Trans. A, **21A** (1990) 2897, and Bulletin of Alloy Phase Diagrams, vol. **5**, No. 2, 1984, p.144.

20) K. Ichimura, N. Inoue, K. Ashida, K. Watanabe and T. Takeuchi, J. Nucl. Mater., **128&129** (1984) 876, K. Ichimura, N. Inoue, K. Watanabe and T. Takeuchi, J. Vac. Sci. Technol., **A2** (1984) 1341.

21) K. Watanabe, K. Ichimura, K. Ashida, M. Matsuyama and T. Takeuchi, Fusion Technol., **14** (1988) 729.

22) J. Crank, "The Mathematics of Diffusion (2nd ed.)", Clarendon Press, Oxford, 1975, p.91.

23) K. Watanabe, K. Ashida and M. Sonobe, J. Nucl. Mater., **173** (1991) 294.

24) M. Nagasaka and T. Yamashina, Jpn. J. Appl. Phys. Suppl. 2, Part **1**, (1974) 61.

25) K. Watanabe, M. Matsuyama, K. Ashida and H. Miyake, Ann. Rept. of Tritium Research Center, **8** (1988) 1.

26) K. Watanabe, M. Matsuyama, K. Ashida and H. Miyake, J. Vac. Sci. Technol., **A7** (1988) 2725.