

Solubility of hydrogen in Pd-Dy-Ni ternary alloys

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2001 J. Phys.: Condens. Matter 13 11589

(<http://iopscience.iop.org/0953-8984/13/50/317>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.238

The article was downloaded on 17/05/2010 at 04:41

Please note that [terms and conditions apply](#).

Solubility of hydrogen in Pd–Dy–Ni ternary alloys

S Anuradha¹, R Sivakumar and S Ramaprabhu²

Department of Physics, Alternative Energy Technology and Magnetic Materials Laboratory,
Indian Institute of Technology, Madras-600 036, India

E-mail: ramp@mmm.iitm.ernet.in

Received 10 May 2001, in final form 17 July 2001

Published 30 November 2001

Online at stacks.iop.org/JPhysCM/13/11589

Abstract

The hydrogen solubility properties of solid-solution ternary Pd_{1-x-y}Dy_xNi_y ($x = 0.020, 0.040$; $y = 0.0555, 0.111$) alloys are investigated in the ranges $473 \leq T (K) \leq 873$ and $0.05 \leq P(\text{bar}) \leq 25$ respectively. From the lattice parameters of the alloys and the thermodynamic parameters of the alloy–hydrogen system, it has been found that the hydrogen solubility properties of these alloys are determined mainly by electronic effects. The relative partial molar enthalpy in the two-phase region implies that hydrogen atoms have a preference towards occupation of the interstitial sites surrounded mostly by Ni atoms.

1. Introduction

The study of hydrogen solubility in Pd and Pd-based alloys has been of fundamental interest because a large amount of hydrogen can easily be dissolved in octahedral interstitial sites of fcc Pd, binary Pd_{1-x}Z_x and ternary Pd_{1-x-y}Z_xZ'_y solid-solution alloys. Many metals dissolve in Pd forming binary and ternary solid-solution alloys. The metals Ag, Au, B, Th, Zr, Sn, Pb, Pt and RE (rare earth) expand the Pd lattice, whereas Fe, Li, Cu, V, Ti, Co, Ni and Rh contract the Pd lattice [1]. The range of solubility of various metals in Pd has been determined by means of x-ray diffraction, and the cubic lattice constant a_0 for the binary Pd_{1-x}Z_x and the ternary Pd_{1-x-y}Z_xZ'_y alloys shows a linear increase or decrease with the concentrations x and $(x + y)$ from the lattice constant (a_0) of Pd. The room-temperature a_0 for fcc Pd_{1-x}Z_x solid-solution alloys varies with x as $a_0 = (a_0)_{\text{Pd}} + a_1x$ (in Å) whereas a_0 for ternary Pd_{1-x-y}Z_xZ'_y solid-solution alloys varies with y for a particular x according to $a_0 = (a_0)_{\text{binary}} + a_2y$ (in Å) in which a_1 and a_2 are the expansion or contraction coefficients at a particular concentration.

The permeability and solubility of hydrogen in binary Pd_{1-x}Z_x and ternary Pd_{1-x-y}Z_xZ'_y alloys have been subject to investigation because of their excellent potential as possible hydrogen-purification membrane materials. The commercial hydrogen-purification membrane

¹ Some of this work was previously presented as part of a Master of Science dissertation.

² Corresponding author.

$\text{Pd}_{0.76}\text{Ag}_{0.24}$ has reasonable permeability at moderate temperatures and pressures, large micro-hardness, is workable for fabricating thin-walled tubes, shows resistance to poisoning by other gas mixtures and shows dimensional stability owing to the suppression of the miscibility gap during permeation. However, the significant solid-solution hardening in $\text{Pd}_{1-x}\text{RE}_x$ alloys leading to diffusion membranes mechanically stronger than $\text{Pd}_{0.76}\text{Ag}_{0.24}$ has focused attention on the study of hydrogen solubility of Pd-rich RE solid-solution alloys.

Hydrogen solubility in Pd solid-solution alloy is influenced by the electronic and the elastic interactions between the hydrogen atom and the solute metal atoms [2]. The electronic effect is due to the change in the Fermi level when valence electrons of the solute metal atom are being transferred to the unfilled 4d band of Pd. The elastic effect is due to the lattice expansion or contraction which arises due to the replacement of Pd by the solute metal atoms. The electronic effects of the substituent metal atoms with the same 'effective valence' are expected to lead to nearly equal numbers of electrons in the host Pd lattice. Hence, for the contracted or expanded alloys, with the same valence of the substitutional metals, the hydrogen solubility is mainly determined by the elastic effect. For example, in the $\text{Pd}_{1-x}\text{RE}_x$ 'expanded' alloys, the hydrogen solubility is due to the high reactivity of the substituent RE metal towards hydrogen and due to the larger size of the interstitial sites in $\text{Pd}_{1-x}\text{RE}_x$. In the $\text{Pd}_{1-x}\text{RE}_x$ (Er, Ho, Dy, Y, Gd, Sm) in the ranges $473 \leq T \text{ (K)} \leq 873$ and $10 \leq P \text{ (mbar)} \leq 1000$, the hydrogen solubility increases and the partial molar enthalpy of hydrogen solution at infinite dilution ΔH_{H}^0 becomes more exothermic with increase of x . Also, at a particular value of x , the size of the octahedral interstitial sites in $\text{Pd}_{1-x}\text{RE}_x$ (RE = Er, Ho, Dy, Y, Gd, Sm) alloys increases in the order given above, which accounts for the increase in the hydrogen solubility and exothermicity of hydrogen absorption in the same order [3–5].

A comparison of the hydrogen solubility properties of the ternary alloys $\text{Pd}_{1-x-y}\text{Z}_x\text{Z}'_y$ ($\text{Z} = \text{Ag}$ ($x = 0.05$), $\text{Z}' = \text{Y(Gd)}$ ($y = 0.000$ to 0.063)) with those of the binary alloys $\text{Pd}_{1-x}\text{Y(Gd)}_x$ and $\text{Pd}_{0.76}\text{Ag}_{0.26}$ has shown that the hydrogen solubility and ΔH_{H}^0 in ternary alloys increases with increasing y , and is attributed mainly to increase in the octahedral interstitial hole size r_h and strong Y–H attractive interaction energy $E_{\text{Y-H}}$ [6].

Study of the thermodynamics of dissolved hydrogen in the ternary fcc alloys $\text{Pd}_{1-x-y}\text{Z}_x\text{Er}_y$ [7] has shown that:

- (i) the lattice parameter of the hydrogen-free ternary alloys increases in the same order as in the erbium-free binary alloys the hydrogen concentration and ΔH_{H}^0 for these ternary alloy hydrogen systems also increase in the same order as in the erbium-free binary alloys,
- (ii) the hydrogen solubility and the exothermicity of hydrogen absorption in the ternary alloy $\text{Pd}_{0.903}\text{Cu}_{0.078}\text{Er}_{0.019}$ are found to be higher than those in pure Pd, even though the lattice constant is less.

This is due to the interaction energy being larger for this alloy than for Pd, a dominant factor for the determination of hydrogen solubility. Similarly, the investigation of hydrogen solubility properties in the binary alloy $\text{Pd}_{1-x}\text{Ni}_x$ shows a decrease in hydrogen concentration with increase in Ni content [8]. The P – C isotherms show higher plateau pressures with increase in Ni content, together with an increase in the plateau width. Hydrogen absorption studies on $\text{Pd}_{1-x}\text{Dy}_x$ for various concentrations of Dy show an increase in the low-pressure hydrogen concentration and a decrease in the miscibility gap with increasing Dy content [9]. The relative partial molar enthalpy and relative partial molar entropy at infinite dilution become more negative with increasing concentration of Dy.

For this investigation, the substituting elements were chosen such that one of them expands the Pd lattice (e.g. Dy) and the other one contracts the lattice (e.g. Ni), thus keeping the lattice constant of the alloy the same as that of pure Pd. The lattice constant (a) of the

alloy $\text{Pd}_{1-x}\text{Ni}_x$ varies according to $a = a_0 + a_1x$ in which, a_0 is the lattice constant of Pd and a_1 is a constant ($a_1 = -26.41$) up to the maximum Ni concentration of 30.1 at.% [1] whereas the lattice constant (a') of the alloy $\text{Pd}_{1-x}\text{Dy}_x$ varies according to $a' = a_0 + a'_1x$ where up to 10 at.% Dy, a'_1 is a constant ($=73.24$) [1]. Thus, the alloys $\text{Pd}_{1-x-y}\text{Dy}_x\text{Ni}_y$ ($x = 0.020, 0.040$; $y = 0.0555, 0.111$) were chosen to facilitate comparison of the hydrogen solubility properties with that of pure Pd. Since the lattice constant of $\text{Pd}_{1-x-y}\text{Dy}_x\text{Ni}_y$ ($x = 0.020, y = 0.0555$; $x = 0.040, y = 0.111$) is the same as that of Pd, the difference in hydrogen solubility properties between these alloys and Pd can be ascribed only to the electronic interactions.

2. Experimental procedure

2.1. Preparation and characterization

The alloys $\text{Pd}_{1-x-y}\text{Dy}_x\text{Ni}_y$ ($x = 0.020, 0.040$; $y = 0.0555, 0.111$) were prepared by taking the constituent elements Pd, Dy and Ni in the required proportions and alloyed by melting the mixtures in an arc furnace under an argon atmosphere at 0.5 bar. The alloys were remelted five times, the button being turned upside down after each solidification to ensure homogeneity. The weight loss during the preparation of the alloys was less than 0.5%. The alloys thus prepared were silver-white and ductile. The buttons were then sealed in quartz ampoules and annealed in vacuum for 3 days at 1023 K and then slowly cooled to room temperature. They were pressed to produce sheets and cleaned in acetone before the hydrogen absorption measurements were carried out. The samples were filed to get fine powder and characterized using power x-ray diffraction using Co $K\alpha$ radiation. The lattice constants were evaluated using a least-squares refinement technique.

2.2. Hydrogen solubility

The hydrogen solubility studies of these alloys were carried out employing the pressure–reduction method. The pressure–composition isotherms for $\text{Pd}_{0.9245}\text{Dy}_{0.020}\text{Ni}_{0.0555}$ were drawn for two different sets of pressure and temperature ranges $0.01 \leq P(\text{bar}) \leq 1, 473 \leq T(\text{K}) \leq 873$ and $1 \leq P(\text{bar}) \leq 40, 303 \leq T(\text{K}) \leq 473$ respectively. The pressure–composition isotherms for $\text{Pd}_{0.849}\text{Dy}_{0.040}\text{Ni}_{0.111}$ were drawn for the ranges $1 \leq P(\text{bar}) \leq 30$ and $303 \leq T(\text{K}) \leq 473$. The alloys were activated initially to produce fresh surfaces and hence enhance the kinetics of hydrogen absorption. The samples were degassed at appropriate temperatures before every cycle of hydrogen absorption to remove hydrogen absorbed in the preceding cycle.

3. Results and discussion

3.1. Crystal structure

The powder x-ray diffractograms of the alloys obtained using Co $K\alpha$ radiation show that the alloys crystallize in cubic symmetry with the space group $Fd\bar{3}m$. The lattice constants of the alloys were found to be $3.884 \pm 0.004 \text{ \AA}$ for $\text{Pd}_{0.9245}\text{Dy}_{0.020}\text{Ni}_{0.0555}$ and $3.876 \pm 0.005 \text{ \AA}$ for $\text{Pd}_{0.849}\text{Dy}_{0.040}\text{Ni}_{0.111}$ respectively. As expected, these values are close to the lattice parameter of the Pd element (3.89 Å).

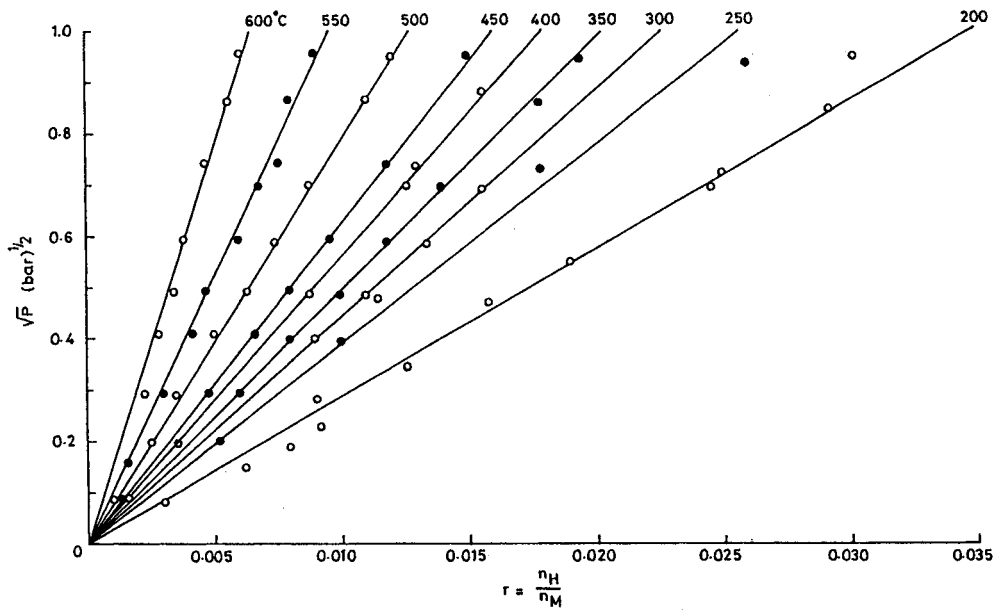


Figure 1. P - C isotherms of $\text{Pd}_{0.9245}\text{Dy}_{0.020}\text{Ni}_{0.0555}$ in the low-pressure range.

3.2. P - C isotherms

The pressure–composition isotherms for $\text{Pd}_{0.9245}\text{Dy}_{0.020}\text{Ni}_{0.0555}$ in the ranges $200 \leq T(^{\circ}\text{C}) \leq 600$ and $0 \leq P(\text{bar}) \leq 1$ are shown in figure 1. It is seen from figure 1 that at very low hydrogen concentrations, Sievert's law is obeyed. Figure 2 shows the pressure–composition isotherms for the same alloy in the ranges $30 \leq T(^{\circ}\text{C}) \leq 200$ and $1 \leq P(\text{bar}) \leq 40$. The isotherms of this alloy exhibit a wavy plateau whereas those of the pure Pd element show a horizontal plateau [9]. This may be attributed to the inhomogeneities of the ternary alloy composition. Examining the isotherms of $\text{Pd}_{0.9245}\text{Dy}_{0.020}\text{Ni}_{0.0555}$ and elemental Pd, it can be seen that there is an upward shift in the plateau pressure. This is accompanied by a reduction in the width of the miscibility gap. The pressure–composition isotherms for the case of $\text{Pd}_{0.849}\text{Dy}_{0.040}\text{Ni}_{0.111}$ in the ranges $30 \leq T(^{\circ}\text{C}) \leq 200$ and $1 \leq P(\text{bar}) \leq 30$ are shown in the figure 3. The plateau pressure at a given temperature for this system is higher than those of Pd–H and $\text{Pd}_{0.9245}\text{Dy}_{0.020}\text{Ni}_{0.0555}$ –H systems and the shift in the plateau pressure is due to increasing content of Ni as can be seen from the earlier discussion of the $\text{Pd}_{1-x}\text{Ni}_x$ binary alloys.

3.3. Thermodynamics of dissolved hydrogen

From the van't Hoff equation, the relative partial molar enthalpies (ΔH_{H}) at various hydrogen concentrations are calculated. The configurational entropy of the dissolved hydrogen atoms is calculated from

$$S_{\text{H}}^{\text{C}} = R \ln \left(\frac{\beta - r}{r} \right)$$

with $\beta = 1$ and using $\Delta S_{\text{H}}^{\text{E}} = \Delta S_{\text{H}} - S_{\text{H}}^{\text{C}}$; $\Delta S_{\text{H}}^{\text{E}}$ can be calculated at various hydrogen concentrations. The dependences of ΔH_{H} and $\Delta S_{\text{H}}^{\text{E}}$ on the hydrogen concentration for the case of $\text{Pd}_{0.9245}\text{Dy}_{0.020}\text{Ni}_{0.0555}$ –H are shown in figures 4 and 5 respectively, and that for

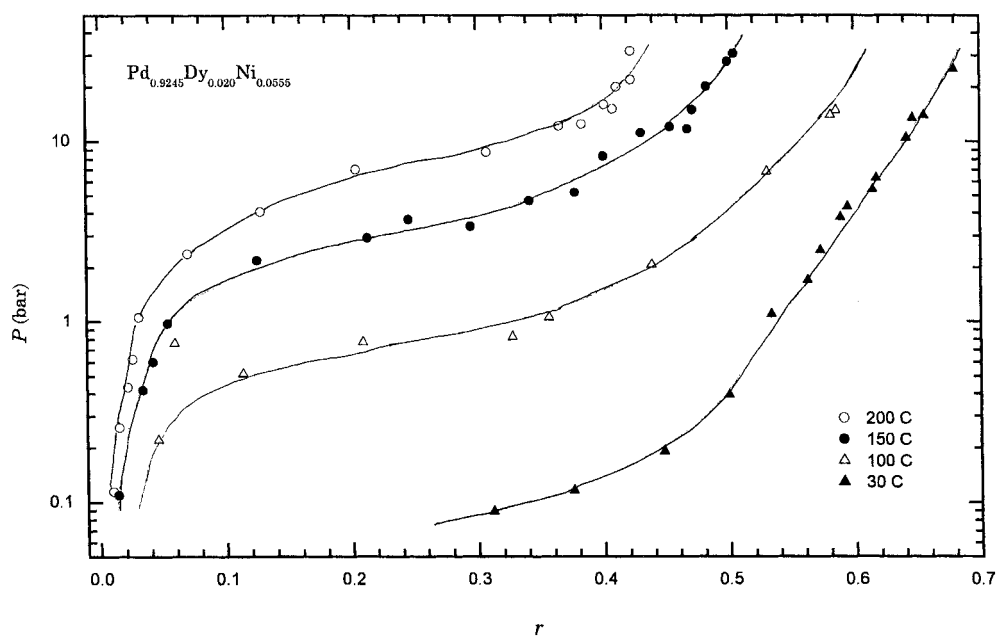


Figure 2. P - C isotherms of the alloy $\text{Pd}_{0.9245}\text{Dy}_{0.020}\text{Ni}_{0.0555}$ in the high-pressure range.

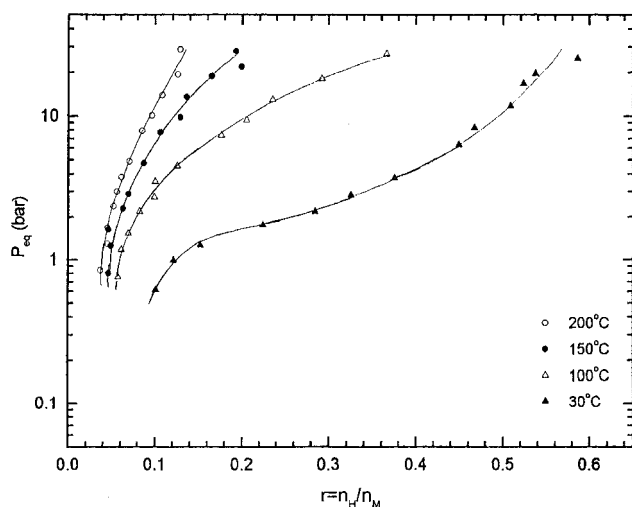


Figure 3. P - C isotherms of the alloy $\text{Pd}_{0.849}\text{Dy}_{0.040}\text{Ni}_{0.111}$.

$\text{Pd}_{0.849}\text{Dy}_{0.040}\text{Ni}_{0.111}$ -H is shown in figure 6. The relative partial molar enthalpy at infinite dilution (ΔH_{H}^0) and the relative partial molar excess enthalpy at infinite dilution ($\Delta S_{\text{H}}^{E,0}$) were obtained using the relations $\Delta H_{\text{H}} = \Delta H_{\text{H}}^0 + a_{\text{H}}r$ and $\Delta S_{\text{H}}^E = \Delta S_{\text{H}}^{E,0} + b_{\text{H}}r$. The values of these parameters along with the values for the Pd-H system are listed in table 1. It can be seen that the values of ΔH_{H}^0 and $\Delta S_{\text{H}}^{E,0}$ are more negative than that of pure Pd, indicating greater exothermicity of the reaction in the present system. Figure 7 shows the dependence of ΔH_{H}^0 on x in $\text{Pd}_{1-x}\text{Dy}_x(\text{Ni}_x)$ -H along with those for the present alloy

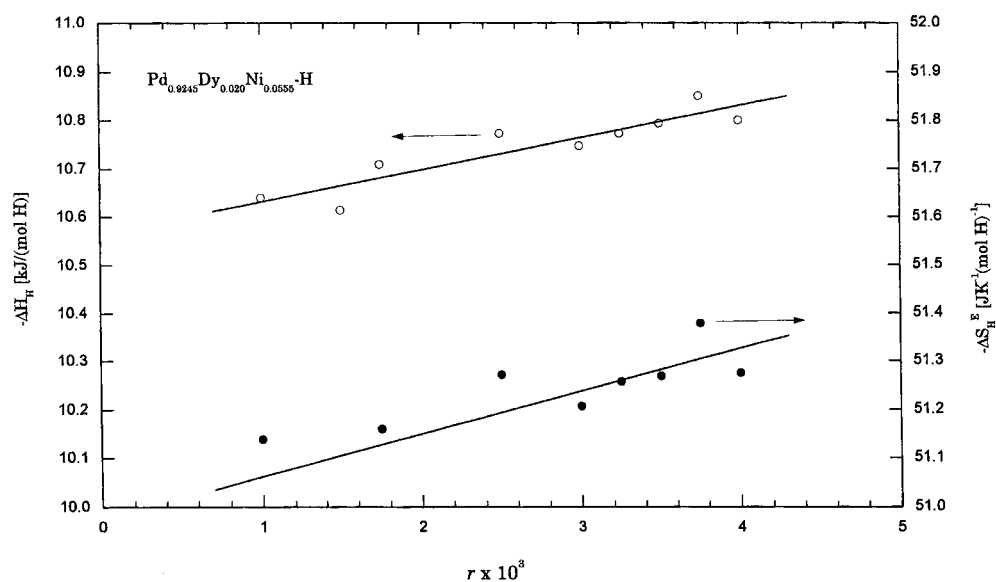


Figure 4. Dependences of ΔH_H and ΔS_H^E on hydrogen concentration in the low-pressure region for $\text{Pd}_{0.9245}\text{Dy}_{0.020}\text{Ni}_{0.0555}\text{-H}$.

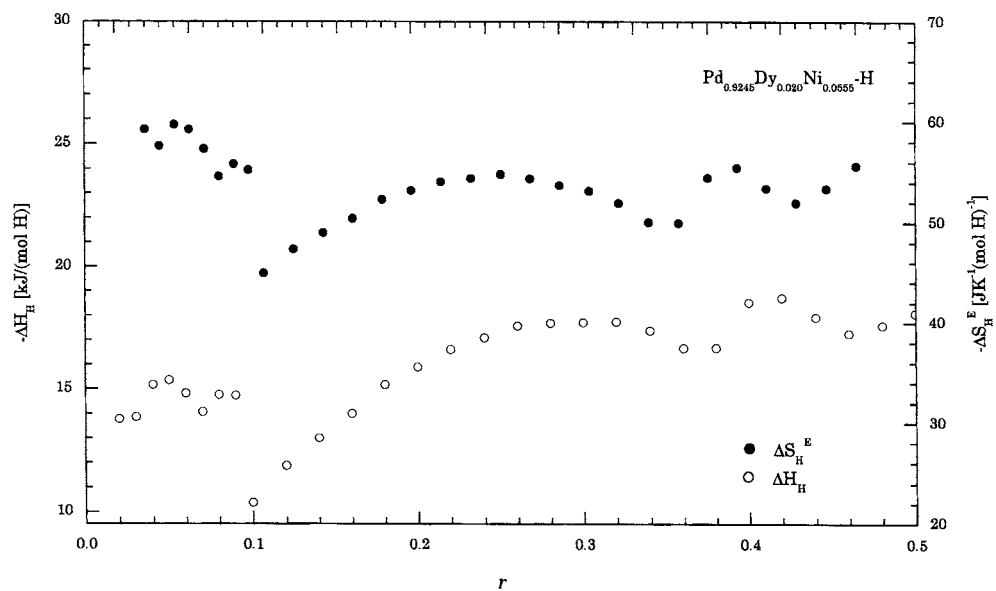


Figure 5. Dependences of ΔH_H and ΔS_H^E on hydrogen concentration in the high-pressure range in $\text{Pd}_{0.9245}\text{Dy}_{0.020}\text{Ni}_{0.0555}\text{-H}$.

hydrides [8, 9]. It is observed that the relative partial molar enthalpies at infinite dilution of $\text{Pd}_{0.9245}\text{Dy}_{0.020}\text{Ni}_{0.0555}$ and $\text{Pd}_{0.849}\text{Dy}_{0.040}\text{Ni}_{0.111}$ lie between those of $\text{Pd}_{1-x}\text{Ni}_x\text{-H}$ and $\text{Pd}_{1-x}\text{Dy}_x\text{-H}$, and closer to that of $\text{Pd}_{1-x}\text{Ni}_x\text{-H}$.

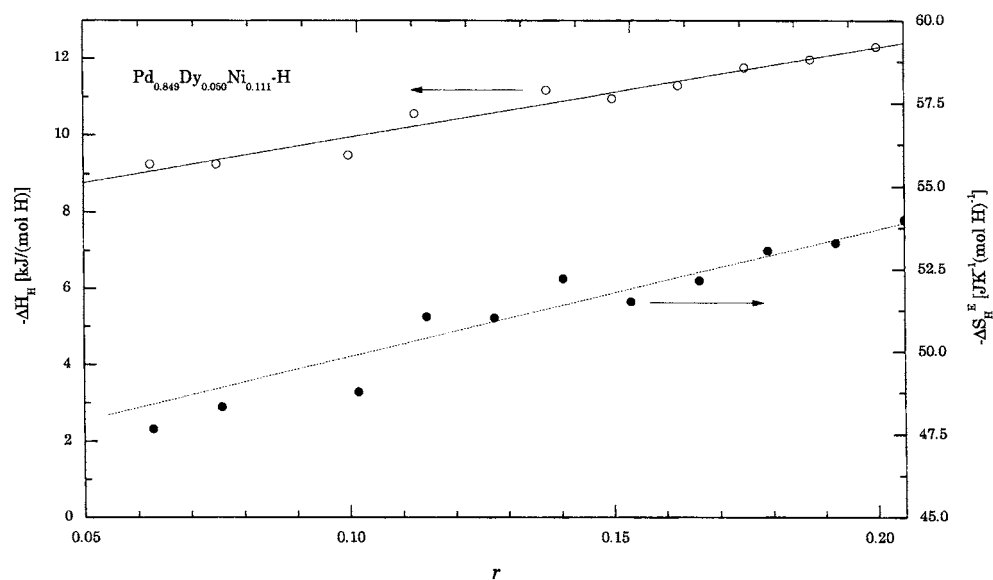


Figure 6. Dependences of ΔH_H and ΔS_H^E on hydrogen concentration in $\text{Pd}_{0.849}\text{Dy}_{0.050}\text{Ni}_{0.111}\text{-H}$.

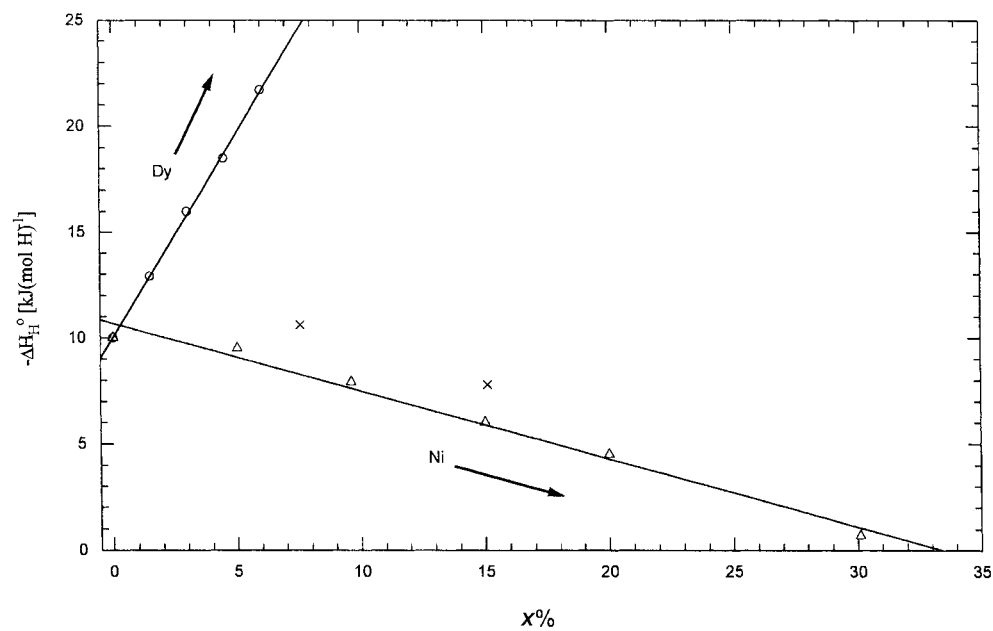


Figure 7. Variations of ΔH_H^0 and ΔS_H^0 with Dy and Ni content in $\text{Pd}_{1-x}\text{Dy}_x(\text{Ni}_x)\text{-H}$.

4. Conclusions

The value of ΔH_H^0 for the $\text{Pd}_{0.9245}\text{Dy}_{0.020}\text{Ni}_{0.0555}\text{-H}$ system is more negative than that of Pd, showing enhanced hydrogen solubility properties despite the fact that the lattice constant of the alloy is almost the same as that of pure Pd. The isotherms of the same alloy–hydrogen system, at

Table 1. Comparison of thermodynamic parameters of the alloy hydrides with Pd–H.

Metal/alloy	Method	$-\Delta H_{\text{H}}^0$ (kJ(mol H) ⁻¹)	$-\Delta S_{\text{H}}^{E,0}$ (J K ⁻¹ (mol H) ⁻¹)
Pd	—	10.0	54.0 [10, 11]
Pd _{0.9245} Dy _{0.020} Ni _{0.0555}	van't Hoff plot	10.6	50.08
Pd _{0.849} Dy _{0.040} Ni _{0.111}	van't Hoff plot	7.8	46

any particular temperature, show that the plateau pressure is higher than that for the Pd element. Because the values of ΔH_{H}^0 in the ranges $0.01 \leq P$ (bar) ≤ 1 and $200 \leq T$ (°C) ≤ 600 lie fairly close to that of Pd_{1-x}Ni_x (figure 7), we can say that the hydrogen atoms have a preference towards occupation of the interstitial sites occupied mostly by Ni atoms. This study revealed that the hydrogen solubility properties of Pd_{0.9245}Dy_{0.020}Ni_{0.0555} and Pd_{0.849}Dy_{0.040}Ni_{0.111} are determined only by the electronic effects. The isotherms of the Pd_{0.849}Dy_{0.040}Ni_{0.111}–H system indicate a decrease in the plateau width when compared to that for Pd. The higher plateau pressure of this alloy–hydrogen system is due to increasing content of Ni.

References

- [1] Weiss A, Ramaprabhu S and Rajalakshmi N 1997 *Z. Phys. Chem., NF* **199** 165
- [2] Ramaprabhu S 1998 *Int. J. Hydrog. Energy* **23** 787
- [3] Ramaprabhu S, Leiberich R and Weiss A 1989 *Z. Phys. Chem., NF* **161** 83
- [4] Ramaprabhu N R S and Weiss A 1989 **93** 686
- [5] Nirupama C V, Sunita and Ramaprabhu S 1997 *J. Alloys Compd.* **255** 142
- [6] Sakamoto Y, Ishimaru N and Inoue Y 1992 *Ber. Bunsenges. Phys. Chem.* **96** 128
- [7] Sanabary F E, Ramaprabhu S and Weiss A 1993 *Ber. Bunsenges. Phys. Chem.* **97** 607
- [8] Sakamoto Y, Matsuo T, Sakai H and Flanagan T B 1989 *Z. Phys. Chem., NF* **162** 89
- [9] Chen F L, Sakamoto Y and Flanagan T B 1993 *Ber. Bunsenges. Phys. Chem.* **97** 784
- [10] Kishimoto S, Oates W A and Flanagan T B 1982 *J. Less Common Met.* **88** 459
- [11] Kuji T, Oates W A, Bowerman B S and Flanagan T B 1983 *J. Phys. F: Met. Phys.* **13** 1785