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Thermodynamic properties for solution of hydrogen in Pd–Pt–Rh ternary alloys

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Abstract

The hydrogen absorption properties of well-annealed $Pd_{100-2x}Pt_xRh_x$ ternary solid solution alloys with x(at.%)=1.5, 3.0, 4.5, 6.0 and 7.5 have been investigated at temperatures between 273 K and 433 K and pressures up to 133.32 kPa by means of pressure–composition isotherm measurements. The room temperature lattice parameters of the hydrogen-free ternary alloys decrease with increasing solute metal content, $x_u = x_{Pt} + x_{Rh}$ with values near the mid-point of the Pd–Pt and Pd–Rh binary alloys. The relative partial molar enthalpy ΔH^0_H at infinite dilution for the ternary alloys becomes less exothermic with solute metal content, and the corresponding entropy ΔS^0_H decreases with increase of solute metal content. Both the values of ΔH^0_H and ΔS^0_H for the ternary alloys with about $x \leq 3.0$ are close to that of Pd–Pt binary alloys. The β-phase hydride in the ternary alloys becomes more unstable with increasing solute metal content, and the standard free energy change, ΔG^0_{plat} at 298 K for hydride formation is nearly at the mid-point between those for the binary alloys.

Keywords: Hydrogen solution; Thermodynamics; Pd–Pt–Rh ternary alloys

1. Introduction

The solubility of hydrogen as reflected in the relative chemical potential $\Delta\mu^0_H$ of dissolved hydrogen at infinite dilution and the formation of β-hydride in Pd binary alloys can be associated mainly with the difference in the strain energy due to the expansion of the Pd lattice for hydrogen occupation, although there are some exceptions [1,2] to the lattice ‘‘expanded’’–‘‘contracted’’ classification of Pd binary alloys.

The present study examines the thermodynamic properties for absorption of hydrogen by $Pd_{100-2x}Pt_xRh_x$ ternary alloys with up to $x=7.5$ at.%. For Pd–Pt binary alloys, a Pt atom expands slightly the Pd lattice, however with regard to hydrogen solution [2,3], the binary alloys behave clearly as contracted rather than expanded alloys. The exceptional behavior of the Pd–Pt alloys may be attributed to the smaller compressibility of Pt compared to Pd [4]. Pd–Rh alloys behave as a contracted alloy since Rh contracts the Pd lattice. The Pd–Rh–H system is, however, one of the few Pd-rich alloys where the β-phase solubility of hydrogen increases with increase of Rh [5–7]. This may be due to the effective valency of the Rh of −1 in Pd as established from the experimental spin paramagnetic susceptibility on Pd–Rh alloys [8]. Thiebaut et al. [9] have recently studied the absorption of deuterium by $Pd_{100-x-y}Pt_xRh_y$ alloys with $0 \leq x$, $y \leq 10$ at.% using different alloy compositions than the present ones; they reported that the absorption pressures depend on the global solute metal content (Pt+Rh) but not on the Pt/Rh ratio.

2. Experimental details

The ternary alloys $Pd_{100-2x}Pt_xRh_x$ with x(at.%)=1.5, 3.0, 4.5, 6.0 and 7.5 were prepared as before [10]. Foil samples of about 50 to 80 μm thickness were annealed at 1123 K for 2 h in vacuo. The lattice parameters a_{ss} of the hydrogen-free alloys were measured by X-ray diffraction and of $a_{\alpha max}$ and $a_{\beta min}$ at the phase boundary compositions of the (α+β) miscibility gaps for alloys hydrogenated electrolytically [11] have also been determined. Hydrogen absorption isotherms were determined between 273 K and 433 K and at hydrogen pressures up to 1000 Torr (133.32 kPa) using a Sieverts-type apparatus.

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Table 1
The room temperature lattice parameters a_{ss} of the hydrogen-free $Pd_{100-2x}Pt_xRh_x$ alloys, together with those at the α_{max} and β_{min} phase boundaries in the $Pd_{100-2x}Pt_xRh_x$–H systems

Alloys	a_{ss}±0.0001 (nm)	$a_{\alpha max}$ (nm)	$a_{\beta min}$ (nm)
Pd	0.3890	0.3895±0.0001	0.4025±0.0001
$Pd_{100-2x}Pt_xRh_x$			
x=1.5	0.3889	0.3893±0.0001	0.4022±0.0001
x==3.0	0.3888	0.3893±0.0001	0.4012±0.0001
x=4.5	0.3887	0.3893±0.0001	0.3993±0.0002
x=6.0	0.3886	0.3896±0.0002	0.3983±0.0002
x=7.5	0.3884	0.3902±0.0002	0.3974±0.0002

3. Results and discussion

The lattice parameters a_{ss} of hydrogen-free Pd–Pt–Rh ternary alloys are given in Table 1, along with $a_{\alpha max}$ and $a_{\beta min}$ of the hydrogenated alloys. The lattice parameters a_{ss} decrease with solute metal content, $x_u=x_{Pt}+x_{Rh}$, their values are near the mid-points of the component Pd–Pt and Pd–Rh binary alloys. Values of $a_{\alpha max}$ and $a_{\beta min}$ for the ternary alloy-H system increase and decrease, respectively, gradually with increasing x_u, lying between those of each binary alloy-H system [11].

The absorption pressure–composition isotherms for a series of $Pd_{100-2x}Pt_xRh_x$ alloys with x=1.5, 3.0, 4.5, 6.0

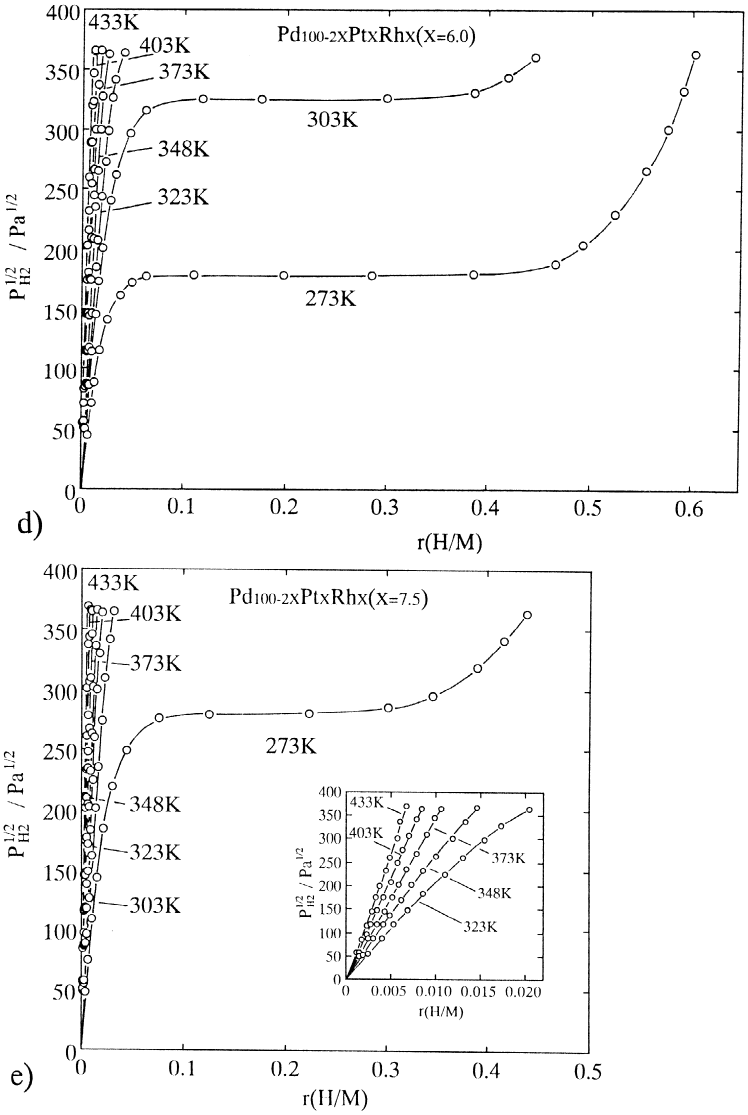

Fig. 1. Pressure–composition isotherms for hydrogen absorption by $Pd_{100-2x}Pt_xRh_x$ alloys: (a) x=1.5; (b) x=3.0; (c) x=4.5; (d) x=6.0; (e) x=7.5.

and 7.5 are shown in Fig. 1(a to e). The low pressure solubilities decrease with increase of solute metal content; the solubilities are larger than found in Pd–Rh binary alloys [6] and smaller than in Pd–Pt binary alloys [2]. The (α+β) plateau pressures p_{plat} for the ternary alloys increase with the solute metal content; the p_{plat} values are smaller than those for the Pd–Pt binary alloys [2] under the same conditions. The higher pressure solubilities in the ternary alloys decrease with x_u, and the solubilities, e.g., at 133.32 kPa, are smaller than those in Pd–Rh [7] and larger than those in Pd–Pt [2] binary alloys.

The relative chemical potential $\Delta\mu_H^0$ of dissolved hydrogen at infinite dilution was obtained from the intercepts of plots of $RT\ln p_{H2}^{1/2}(1-r)/r$ vs. r and the apparent H–H pair interaction free energies g_1 between dissolved hydrogen were determined from the slopes of the plots. The relative partial molar enthalpy ΔH_H^0 and entropy ΔS_H^0 of solution of hydrogen at infinite dilution were determined from temperature dependence of $\Delta\mu_H^0$ values. The derived thermodynamic parameters in the ternary alloys are summarized in Table 2.

Fig. 2 shows plots of $\Delta\mu_H^0$ at 298 K against atom fraction x_u, in comparison with the previously determined data for the Pd–Pt [2] and Pd–Rh [7] binary alloys. The dissolved hydrogen in the dilute phase region in the ternary alloys becomes more unstable with increasing solute metal content, lying between the values of each binary alloy, however the alloy composition dependence of the $\Delta\mu_H^0$ values for the ternary alloys are near to those for Pd–Pt binary alloys rather than the Pd–Rh binary alloys. The apparent H–H attractive pair interaction energy g_1 for the ternary alloys at 348 K (Table 2) decreases with increasing x_u; this trend is similar to that for each binary alloy [2,7].

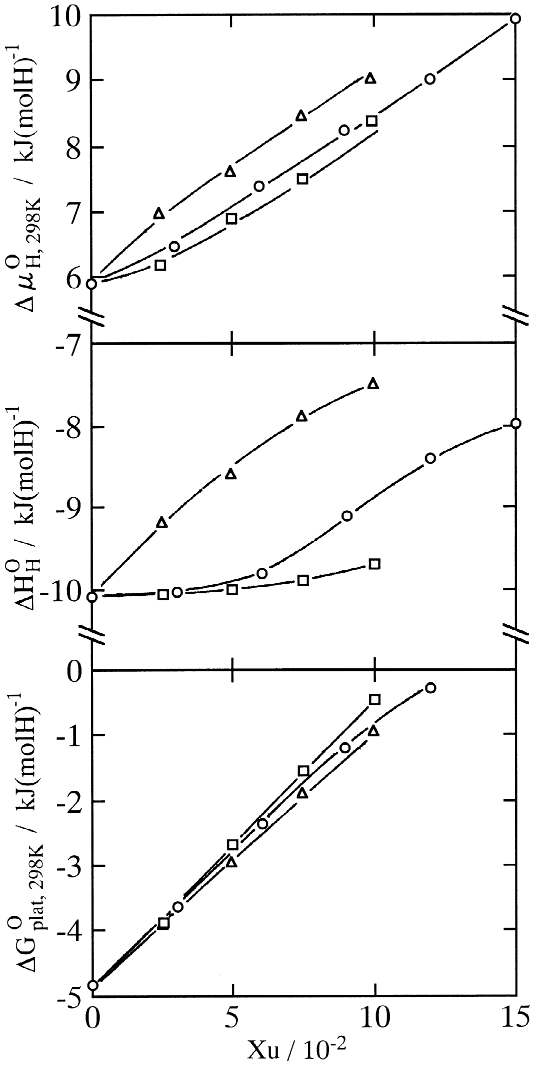

Fig. 2. Plots of $\Delta\mu^0_{H,298\ K}$, ΔH^0_H and $\Delta G^0_{plat,298\ K}$ at 298 K vs. atom fraction x_u for $Pd_{100-2x}Pt_xRh_x$ alloys, compared with those of the previously determined Pd–Pt and Pd–Rh binary alloys: ○, $Pd_{100-2x}Pt_xRh_x$; △, Pd–Rh [7]; □, Pd–Pt [2].

Fig. 2 also shows plots of ΔH_H^0 vs. x_u for the ternary alloys, in comparison with those of each binary alloy. The relative partial molar enthalpy ΔH_H^0 at infinite dilution for the $Pd_{100-2x}Pt_xRh_x$ alloys becomes less exothermic with solute metal content, and at the same alloy composition, the ΔH_H^0 values are less exothermic than that for Pd–Pt binary alloys [2], however for the alloys with about $x \leq 3.0$ the values are close to that of Pd–Pt binary alloys [2]. The reason for the fact that the ΔH_H^0 values for the ternary alloys are near those of the Pd–Pt binary alloys, especially for alloys with $x \leq 3.0$, may be related to the selective occupation of Pd-rich interstices near Pt atoms rather near than Rh atoms, because of a smaller strain energy necessary for hydrogen occupation of the interstices. The corresponding entropy $\Delta S_H^0(\beta=1)$ (Table 2) for the ternary

Table 2
Thermodynamic parameters of hydrogen absorption by $Pd_{100-2x}Pt_xRh_x$ alloys

Specimens	ΔH_H^0 [kJ (mol H)$^{-1}$]	ΔS_H^0 [J (mol H)$^{-1}$]	g_1^* [kJ (mol H)$^{-1}$]	ΔH_{plat}^0 [kJ (mol H)$^{-1}$]	ΔS_{plat}^0 [J (mol H)$^{-1}$]	ΔH_{solv}^z [kJ (mol H)$^{-1}$]	ΔS_{solv}^z [J (mol H)$^{-1}$ K^{-1}]
Pd	−10.1	−53.7	−47.3	−18.4	−45.5	10.7	2.3
$Pd_{100-2x}Pt_xRh_x$							
$x=1.5$	−10.0	−55.4	−37.2	−17.6	−46.9	10.1	3.2
$x=3.0$	−9.8	−57.7	−36.3	−16.4	−47.1	9.2	2.8
$x=4.5$	−9.1	58.2	−33.4	−14.5	−44.6	8.9	5.0
$x=6.0$	−8.4	−58.4	−19.5	−12.4	40.7	8.8	7.4
$x=7.5$	−8.0	−60.1	−10.8				

* at $T=348$ K and $\beta=1$

alloys decreases with increase of solute metal content as it does for each binary alloy, however, the values for the alloys with $x \leq 3.0$ are also close to that of Pd–Pt binary alloys [2].

The plateau and solvus thermodynamic parameters obtained from temperature dependences of the plateau pressures and the solvus compositions, respectively in the alloys are given in Table 2. The standard enthalpy changes $\Delta H^0_{\mathrm{plat}}$ for hydride formation become less exothermic with solute metal content, whereas the values of $\Delta S^0_{\mathrm{plat}}$ show a minimum for the alloys with about $x=3.0$. Fig. 2 also shows the standard free energy change $\Delta G^0_{\mathrm{plat,298\ K}}$ at 298 K for β-hydride formation against the solute metal content, in comparison with those for each binary alloy [2,7]. It can be seen that the β-hydride in the ternary alloys becomes less stable with increase of solute metal content, lying near the mid-points between those of each binary alloy [2,7], where the hydride for the latter alloys is more stable than that of the former alloys.

As can be seen from the solvus thermodynamic data of $\Delta H^{\mathrm{z}}_{\mathrm{solv}}$ and $\Delta S^{\mathrm{z}}_{\mathrm{solv}}$ (Table 2) for the α_{max} phase boundary formation, the hydrogen solubility limit at the same temperature in the α-phase of the ternary alloys increases regularly with solute metal content, independently of their lattice-expanding or -contracting properties. The result is similar to the lattice expansion at the α_{max} composition determined by X-ray diffraction (Table 1).

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