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Calorimetric enthalpies for the reaction of H_2 with Pd–Cu alloys at 303 K

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Abstract

Thermodynamic parameters for the reaction of H_2 with $Pd_{1-x}Cu_x$ ($x=0$, 0.05, 0.096, 0.15, 0.2 and 0.3) alloys have been determined via reaction calorimetric and isotherms measurements at 303 K. Both the hydrogen solubilities in the dilute phase and the lengths of the plateaux decrease with increase of x, while the plateau pressures increase with increase of x. The magnitude of the enthalpies for the plateau reaction decreases with increase of x. In the single hydride phase region at the end of the plateau the $|\Delta H_H|$ values decrease with H content. Relative entropies have been determined from the enthalpies and the equilibrium pressures. The entropies for the plateau reaction do not change very much with x in $Pd_{1-x}Cu_x$

Keywords: Hydrogen absorbing materials; Pd–Cu alloys; Gas–solid calorimetry

1. Introduction

The absorption of H_2 by Pd–Cu alloys has been investigated by several groups using pressure–composition–temperature (P–C–T) data [1–4]. The plateau pressures increase and the H capacity of the alloys decrease with mol fraction Cu, x, which, in most cases, is consistent with the decrease of the lattice parameters decrease with x [1,2,4], i.e. these alloys have contracted unit cells with respect to Pd and it would be expected that the plateau pressures would increase with x [5]. For Pd–Cu alloys the critical composition for two phase formation is $x=0.29$ at 303 K [1].

Kleppa et al. [6] determined calorimetric enthalpies at dilute H contents for several Pd–Cu alloys at 555 K. They found that the relative partial molar enthalpy magnitudes decrease with x. In this investigation similar calorimetric studies will be carried out but at ambient temperature where enthalpies can be determined over a wide range of H contents including the two phase region where the dilute↔hydride phase transitions take place. The enthalpies for the plateau reaction are available for absorption up to $x=0.20$ from (P–C–T) data [4]. It will be of interest to compare the Pd–Cu–H system with the other members of the group IB solutes, i.e. Ag and Au, where data are available [7,8].

2. Experimental

The pure elements were arc-melted together forming buttons which were annealed at 1133 K for 72 h. They were then rolled into foil of about 100 μm thickness and annealed for a further 24 h at 1133 K. The following alloys were prepared: $x=0.05$, 0.10, 0.15, 0.20, and 0.30. The foils (≈1.5 g total) were cut into small pieces of about 40×50 μm and mixed with 3 g of finely divided Cu for improved thermal conductivity needed for the calorimetry. The heat-leak, dual cell calorimeter has been described elsewhere [9]. The calorimetric measurements and accompanying isotherms were carried out at 303 K.

3. Results and discussion

3.1. Dilute phase solubilities

The dilute phase solubilities (303 K) are shown in Fig. 1. The terminal hydrogen solubilities increase with x as has been observed for all other binary Pd-rich alloys [5]. The solubility at a given p_{H2} decreases with x as expected for a contracted Pd alloy. Relative partial molar enthalpies, ΔH_H, have been measured calorimetrically in the dilute phase but there was too much scatter to obtain meaningful results and the values from Burch and Buss [1] and Sakamoto et al. [4] are shown in Table 1 instead where both sets of enthalpies decrease in magnitude with x as expected. If it is assumed that there are no changes in

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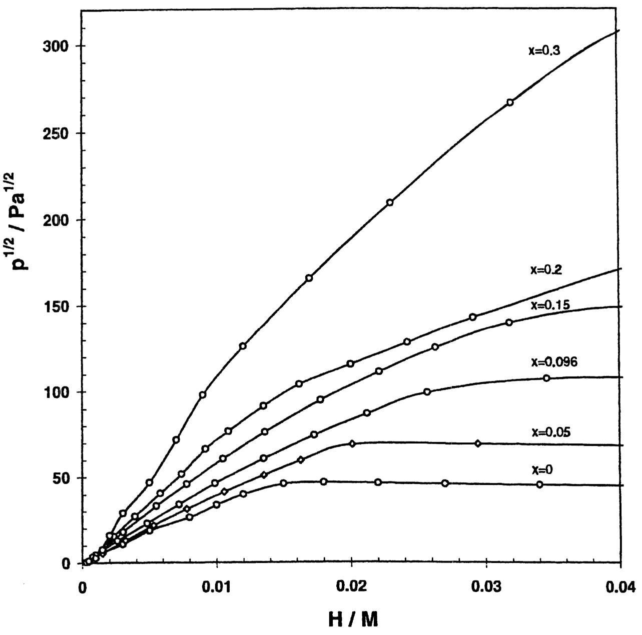

Fig. 1. H_2 solubilities in the dilute phase in Pd–Cu alloys (303 K).

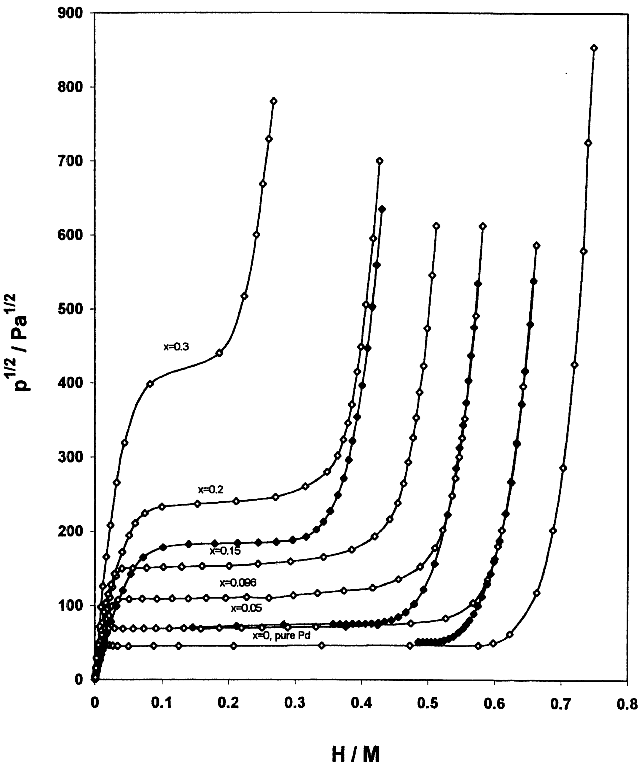

Fig. 2. Complete H_2 isotherms for Pd–Cu alloys at 303 K. Open and filled symbols for absorption and desorption, respectively.

ΔS^0_H with x, then the values of ΔH^0_H can be determined at small r=H/M (atom ratio) in the ideal range from the relation $\Delta H^0_H = RT \ln p^{1/2}_{H2} + T\Delta S^0_H - r \ln [r/(1-r)]$ [10]; $\Delta S^0_H = -55$ J/K mol H, i.e. the value for Pd–H. The values derived here fall between those given by Burch and Buss [1] and Sakamoto et al. [4], e.g. for the $x=0.15$ alloy this method gives −8.6 kJ/mol H whereas the average of the two from Table 1 is −8.7 kJ/mol H. This indicates that the changes of ΔS^0_H with x are not very large in agreement with Sakamoto et al. [4] rather than Kleppa et al. [6]. Burch and Buss [1] found that, although ΔS^0_H decreased with x, the decrease was much smaller than for Pd–Ag alloys.

3.2. Complete isotherms and calorimetrically determined parameters

It can be seen in Fig. 2 that the plateau pressures increase with x and the plateau breadths decrease so that the two phase region disappears at about $x=0.30$ in good agreement with the results of Burch and Buss [1] (303 K). A linear relationship between p_{plat} and x does not obtain but there is one between log p_{plat} and x (Fig. 3) where the former is proportional to the free energy change for reaction (1):

$$1/2H_2 + [1/(b-a)]MH_a \rightarrow [1/(b-a)]MH_b \qquad (1)$$

which takes place in the two phase, plateau region. The plot in Fig. 3 shows that hysteresis vanishes at about $x=0.30$ confirming the estimation from Fig. 2 and close to $x=0.29$ given by Burch and Buss [1].

Enthalpies were determined over the whole of the accessible range of H contents up to about 10 bar (303 K). In the two phase regions they are relative integral molar

Table 1
A summary of the thermodynamic parameters for the $Pd_{1-x}Cu_x$ system (303 K)

x	r_α	r_β	p_f (kPa)	p_d (kPa)	$\lvert\Delta H^0_H\rvert$	$\lvert\Delta H_{\text{plat}}\rvert$	$\lvert\Delta S_{\text{plat}}\rvert$	Hysteresis
0	0.015	0.72	2.17	1.15	10.2	19.2	46.1	800
0.05	0.012	0.65	4.99	2.60	9.9 (8.9)	17.6	44.3	821
0.096	0.010	0.57	12.16	5.98	9.6 (8.7)	16.3	43.5	894
0.15	0.008	0.48	23.58	11.04	9.2 (8.2)	15.0	41.9	956
0.20	0.007	0.39	56.58	33.70	8.3 (8.0)	14.2	43.4	653
0.30	0.005	0.21	163.3	154.1	–	11.8	40.8	73

The dilute and hydride phase solubilities shown in columns 2 and 3 have been determined at 0.02 and 2.0 bar H_2, respectively, the units of the enthalpies are kJ/mol H, the entropy is J/K mol H and hysteresis is measured by $RT \ln (p_f/p_d)^{1/2}$ in kJ/mol H. The ΔH^0_H values are from Ref. [4] and those in parentheses from Ref. [1].

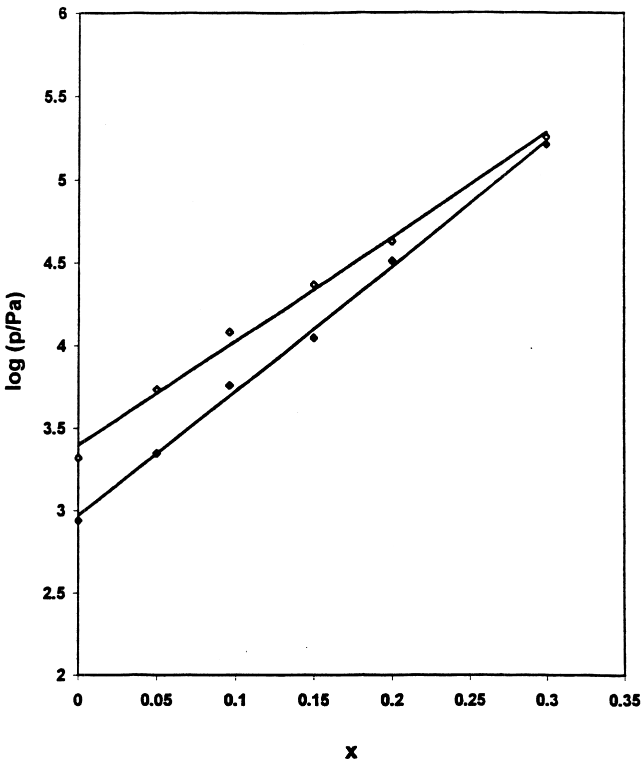

Fig. 3. Plots of log p_f and log p_d as a function of x (303 K).

enthalpies and in the dilute and hydride single phase regions they are relative partial molar enthalpies. Some plots of enthalpy as a function of r are shown in Figs. 4 and 5. The former shows enthalpies for absorption and the latter for desorption.

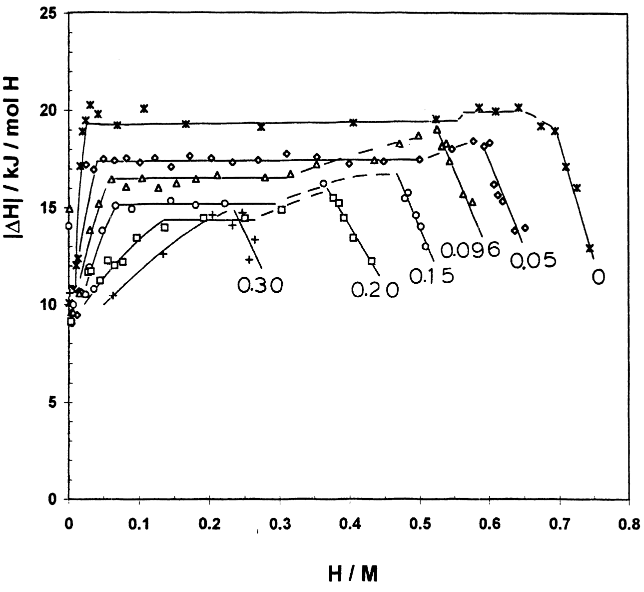

Fig. 4. Calorimetrically measured enthalpies of absorption over the complete range of H contents (303 K). The numbers on the plots indicate x of the alloy.

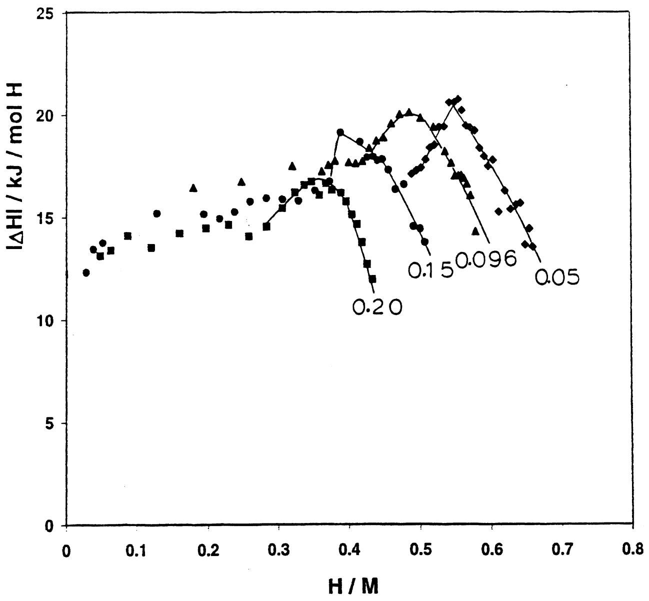

Fig. 5. Calorimetrically measured enthalpies of desorption over the complete range of H contents (303 K). The numbers on the plots indicate x of the alloy.

The enthalpies in the plateau regions should be the same magnitude for absorption and desorption [9,11] and any deviation from this is due to experimental error. This is the case for the $x = 0.20$ but for the 0.15 alloy there seems to be a difference between absorption and desorption values in the latter half of the isotherm for unknown reasons but for $x = 0.096$ there is little difference between absorption and desorption in the plateau region. At the high end of the plateau regions, however, there is a difference between absorption and desorption which was also observed for Pd–H(D) [9] which is due to two factors: (i) there is a maximum in $|\Delta H_H|$ which is hidden by the plateau region and (ii) the phase boundary $(\alpha + \beta)/\beta$ has a larger content b' than the phase boundary, $\beta/(\alpha + \beta)$, during decomposition, b'', which is a result of hysteresis. Consequently at some H contents, the enthalpies for H_2 desorption reflect single phase partial molar enthalpies which are decreasing in magnitude from a maximum while at the same contents, the absorption enthalpies are integral plateau values. This is seen, for example, in Fig. 6 for the $x = 0.05$ alloy where the desorption data show a higher maximum than the absorption data and the phase boundary for desorption is located at about halfway down the 'hill' on the low H content side, i.e. about $r = 0.52$. The data for this alloy also show the expected discontinuity in enthalpies in the transition from the dilute to the plateau region [9]. Desorption data were not obtained very far along the plateau because of the low p_{H2} of the desorption plateau.

$|\Delta H_H|$ values decrease with r at the end of the plateau regions for all of the alloys (Figs. 4–6) which indicates that the solubility in these alloys is limited mainly by enthalpy rather than entropy. The trends in the entropies

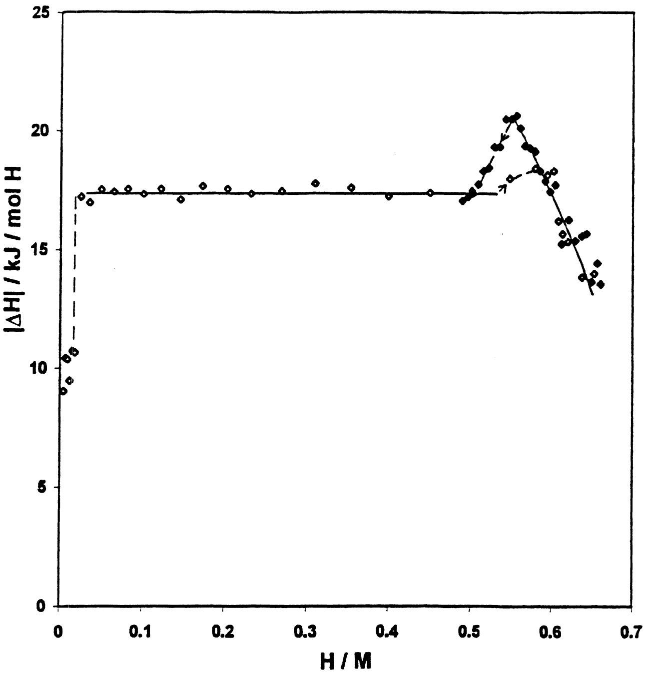

Fig. 6. Calorimetrically measured enthalpies of absorption and desorption for the $x=0.05$ alloy.

are not so clear and there seems to be an increase in $|\Delta S_H|$ and then decrease at the end of the plateau.

4. Conclusions

The change of $|\Delta H_{plat}|$ with x is in the opposite direction from the other Pd—M alloys where M is a member of group 1B. This is because the substitutional solutes Ag and Au expand the Pd lattice whereas Cu contracts it and it is therefore expected that the change of $|\Delta H_{plat}|$ with M will be in the opposite directions as observed. The decrease in H capacity with M is somewhat smaller for Cu than for Ag or Au [7,8]. Due to the present space restraints additional results of this research including results for hydrogen induced changes in the $x=0.25$ and 0.30 alloys at elevated temperatures and p_{H2} will be published later.

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