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Solution of Hydrogen in Palladium/Copper Alloys

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The solution of hydrogen in Pd/Cu fcc substitutional alloys has been examined in the region of low hydrogen contents. Relative partial molar enthalpies of absorption at infinite dilution are found to be somewhat less exothermic for the alloys than for palladium but the change with X_{Cu} is small. Partial excess entropies of absorption decrease with X_{Cu} but not as markedly as for the other Pd/group IB alloys. Relative electrical resistance relationships for Pd/Cu alloys have been determined as a function of their hydrogen contents. Interstitial hydrogen increases the relative electrical resistance to a lesser extent with increase of X_{Cu}, but the absolute increase of resistance is nearly invariant with X_{Cu}.

Introduction

The key position of the Pd/Cu alloy system in the elucidation of the state of hydrogen in palladium alloys has been emphasized by Burch and Buss (*1*) and Flanagan and Chisdes (*2*). In contrast to the other Pd/group IB substitutional alloys, Pd/Cu alloys have smaller molar volumes than palladium, but they have electronic similarities to the Pd/Au and Pd/Ag alloy systems. The Pd/Cu system is therefore of potential importance for the separation of the influences of the electronic and geometric character of palladium alloys upon their hydrogen absorption characteristics. The relative roles of these two factors have been the subject of some controversy in the literature (*3*, *4*). According to Burch and Buss (*1*), despite the fact that copper lies to the right of palladium in the periodic table, the partial enthalpy of absorption of hydrogen at infinite dilution, $\Delta\bar{H}_{H\to 0}$, increases with X_{Cu}, i.e., the alloy system behaves like alloys of palladium with substitutional partners to the left of, or in the same column, as palladium in the periodic table, e.g., Pd/Ir (*5*) or Pd/Rh (*6*). On the other hand, alloys to the right of palladium in the periodic table, other than Pd/Cu, exhibit the opposite trend (*7–9*). The experimental data upon which Burch and Buss (*1*) base this conclusion are rather sparse and similar data have been determined here. They employed samples that were activated towards hydrogen uptake by a coating of palladium black and noted that sluggish equilibria and poisoning occurred even in the presence of such coatings. Flanagan and Chisdes (*2*) employed a different technique i.e., hydrogen was absorbed from H_2-gas-stirred acidic solutions and the course of absorption was followed by electrical resistance and electrode potential changes. These results have been presented in a preliminary report (*2*) and are described here more completely together with data on the relative electrical resistance changes with hydrogen content. Since the preliminary report additional data have been obtained at larger values of X_{Cu} using direct equilibration of hydrogen gas with uncoated Pd/Cu alloys in the form of thin sheets.

Recently there has been a renewed interest in Pd/group IB alloys with regard to their hydrogen absorption characteristics because of the high superconducting transition temperatures observed (*10*). For example, with

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hydrogen-charged Pd/(0.45)Cu a T_c of 16.6°K has been attained (*10*). There is a systematic increase of T_c in passing from Au to Cu in these hydrogen-charged binary alloys and there is a trend of the value of X_M at which the maximum value of T_c is observed, i.e., $X_{Au} = 0.15$, $X_{Ag} = 0.30$, and $X_{Cu} = 0.45$. It has been found that even for a hydrogen-charged alloy with $X_{Cu} = 0.85$, $T_c = 6$ K (*10*). It therefore appears that Pd/Cu alloys will absorb considerable amounts of hydrogen even at very high copper contents, albeit under conditions of proton bombardment. The study of hydrogen absorption by Pd/Cu alloys may help to elucidate these interesting superconductivity trends.

Experimental

Pd/Cu alloys were employed as wires or as thin sheets. The sheets were prepared in this laboratory by arc-melting the pure components. The alloys were then homogenized at 900°C for approximately four days, then rolled into sheets and re-annealed. The weight loss on melting was small and the limits of compositional error (±1 %) were calculated by assuming that either all copper or all palladium was lost during the melting process. The compositions of the alloys were shown to be homogeneous by atomic absorption analysis of several regions of a typical alloy sheet. The analyses agreed well with the compositions estimated from the initial weights. Lattice spacings were determined from X-ray powder patterns made on annealed filings of the alloys. This provided another check on the compositions which are accurate to ±1%; the X-ray spacings are known from other sources (*1*, *11*).

The wire samples were obtained from Engelhard Industries and analyzed by them; these compositions are within ±0.2% of the cited values. These samples were employed to determine the X-ray parameters of hydrogen-containing alloys, the electrical resistance versus hydrogen content relationships, and the equilibrium hydrogen solubilities at 1 atm of H_2.

The techniques employed have been described elsewhere (*5*, *6*). It should be mentioned that the poisoning referred to (*1*), i.e., that the samples frequently had to be reactivated in order to ensure hydrogen equilibrium, was *not* noted for uncoated samples in these studies that were made in a mercury- and grease-free ultra-high vacuum system. Poisoning was, however, frequently encountered in the electrochemical/gas phase technique.

Results and Discussion

X-Ray Measurements

The fcc lattice parameters were determined by X-ray diffraction using a Debye–Sherrer powder camera. Samples were well annealed. Lattice parameters of hydrogen-containing samples were obtained using wires which had been coated with methyl methacrylate after obtaining the desired hydrogen content; the coating prevents hydrogen loss. Results are shown in Table I along with data obtained [see (*1*)] for their hydrogen-free samples.

The lattice parameters agree quite well with those of Burch and Buss (*1*). The parameters of the samples prepared in our laboratories agree with the data of the samples obtained commercially.

Figure 1 shows the envelope of the two-phase parameters, expressed as Δa_0 [$= a_0$(H-containing) $- a_0$(H-free)], plotted against X_{Cu} for alloys containing hydrogen coexisting in

TABLE I

LATTICE PARAMETERS OF H-FREE AND H-CONTAINING Pd/Cu ALLOYS (298°K)

X_{Cu}	a_0(Å)	a_0(Å, α_{max})	a_0(Å, β_{min})
0	3.889	3.895	4.025
0.04	3.879	3.884	4.010
0.08	3.875	—	3.987
0.10	3.868	—	—
0.10 (*1*)	3.865	—	—
0.15	3.856	3.864	3.953
0.18	3.845	—	—
0.20 (*1*)	3.840	—	—
0.23	3.841	3.850	3.917
0.29	3.818	—	—
0.29	3.823	3.834	3.873
0.35	3.807	—	—

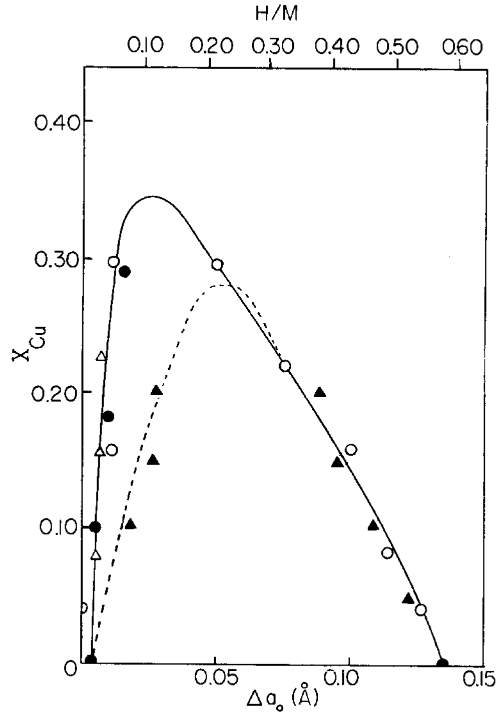

FIG. 1. Phase envelope for Pd/Cu/H estimated from various physical parameters (~ 298°K). ○ = lattice parameter changes, $\Delta a_0[= a_0(n) - a_0(n = 0)]$ plotted against X_{Cu}; ▲, values of two-phase hydrogen contents estimated from absorption isotherms plotted against $H/M = n$, upper scale (*1*); ●, hydrogen contents estimated from absorption isotherms, this research; △, hydrogen contents estimated from R/R_0 versus n data, this research.

the α- and β-phases. Two phases are no longer formed (298°K) at copper contents greater than $X_{Cu} = 0.35$. The sample with $X_{Cu} = 0.29$ was charged with hydrogen electrolytically, since it does not form two phases at pressures of ≤ 1 atm (298°K). The phase envelope extends to a greater atom fraction of substituted metal than for any other palladium alloy system save Pd/Rh (*12*). (Rhodium itself probably absorbs hydrogen at high pressures.)

Changes of Electrical Resistance with Hydrogen Content

Changes of relative electrical resistance (R/R_0) with hydrogen content, expressed as n(H-to-metal atom ratio), have been determined at 298°K. Burch and Buss (*1*) have been the only other workers to determine such data for this alloy system. They reported that the shapes of these relationships are similar to that of pure palladium rather than, for example, Pd/Ag (*13*) or Pd/Au (*14*) alloys. They have also reported that there is no trend in these relationships with X_{Cu}.

These relationships have been very carefully determined in this research for both the α-phase and over the entire range of hydrogen contents available at pressures ≤ 1 atm of H_2. The data were determined by a separate degassing analysis of each set of (R/R_0)-n points. Figure 2 shows the data in the low hydrogen content α-phase at 298°K. Only the experimental points for the $X_{Cu} = 0.08$ alloy are shown and this indicates typical experimental scatter encountered in this region of contents. Data for pure palladium/H_2 are also shown and these data have been taken from (*15*), which are believed to be more accurate than the data given in (*16*). It is clear that there is a trend towards a decreasing effect of hydrogen on R/R_0 as X_{Cu} increases. For comparison, α-phase data are shown for a Pd/(0.16)Au alloy (*14*) and a Pd/(0.054)Pb alloy (*9*). The slopes are seen to be similar for these alloys and $X_{Cu} \sim 0.19$. This suggests that copper and gold have similar effects on changes of R/R_0 whereas lead has roughly four times the effect of these two alloys. It is quite possible that this is related to the donation of one electron by copper and gold to the collective *d* band of palladium whereas on this basis, lead donates ~ 4 electrons.

Rather than examining changes of R/R_0 with n, the absolute changes of resistivity may be determined. Table II shows the resistivities of some Pd/Cu alloys (298°K) and the initial changes of R/R_0 with Δn together with the corresponding changes $\Delta\rho/\Delta n$. The alloys have been annealed *in vacuo* prior to measuring their electrical resistivities. The resistivities were measured in distilled water (298.2°K) by determining the potential drop across the samples with about 2 mA passing through the wire samples. It can be seen that the changes, $\Delta\rho/\Delta n$, are rather constant and slightly smaller than reported for palladium (*15*). The presentation of R/R_0 against n thus introduces

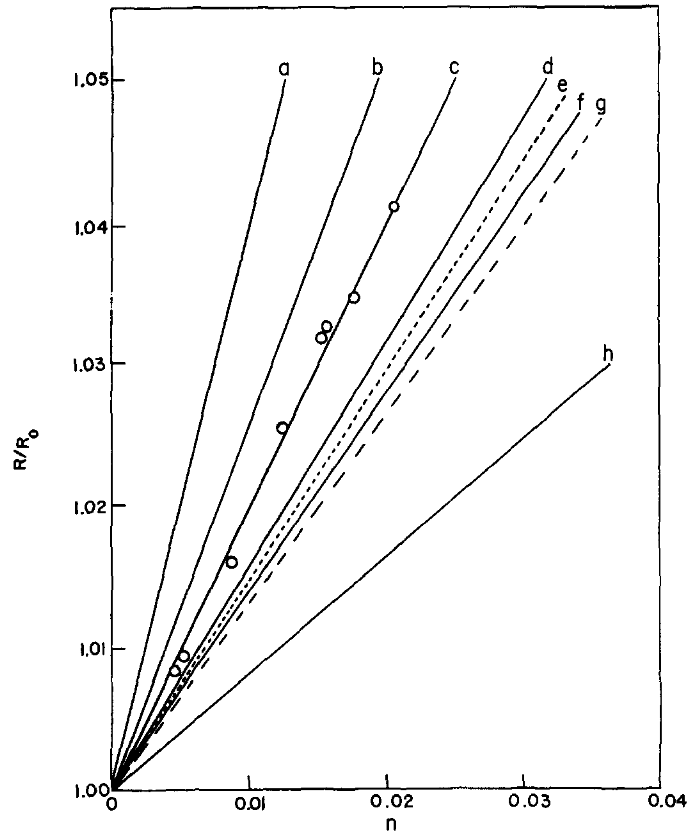

FIG. 2. R/R_0 plotted against n (298°K) in the low hydrogen content α-phase. Curves a, b, c, d, e, f, g, and h represent $X_{Cu} = 0.00$ (*15*), 0.04, 0.08, 0.16, and Pd/(0.16)Au (*14*), $X_{Cu} = 0.23$, Pd/(0.054)Pb (*9*), and $X_{Cu} = 0.29$, respectively. Data are shown for $X_{Cu} = 0.08$ only.

TABLE II

RESISTIVITIES OF SOME Pd/Cu ALLOYS (298°K) AND THE EFFECT OF INTERSTITIAL HYDROGEN IN THE α-PHASE

Alloy (X_{Cu})	ρ_0/ohm-cm	$\Delta R/R_0/\Delta n$	$\Delta\rho/\Delta n$/ohm-cm
0.00	1.10×10^{-5}	4.0	4.4×10^{-5}
0.04	1.58×10^{-5}	2.4	3.8×10^{-5}
0.08	2.05×10^{-5}	1.9	3.8×10^{-5}
0.16	3.03×10^{-5}	1.4	4.2×10^{-5}
0.23	3.78×10^{-5}	1.0	3.8×10^{-5}
0.29	4.23×10^{-5}	0.83	3.5×10^{-5}

changes due to variations of R_0 from alloy to alloy although values of $\Delta\rho/\Delta n$ may be relatively constant. If $(\Delta R/R_0)/\Delta n$ were constant for these alloys as reported (*1*), then $\Delta\rho/\Delta n$ would change dramatically with X_{Cu}.

Because of the convenience in presentation and their usefulness in determining accompanying values of n, the data will be presented as plots of R/R_0 against n, but it should be kept in mind that this representation can mask some facts about the fundamental nature of the resistivity changes when intercomparing alloys. A typical electrical resistance relationship covering the entire range of hydrogen contents available up to 1 atm of H_2 is shown in Fig. 3, and the relationships for all of the alloys studied here are shown schematically in Fig. 4. It can be seen that the trend established in the α-phase carries over into the region of larger hydrogen contents. There is a definite change of slope at the hydrogen content where the hydride phase first appears in the hydrogen-saturated alloy. The greater slope of the pure α-phase implies that the effect

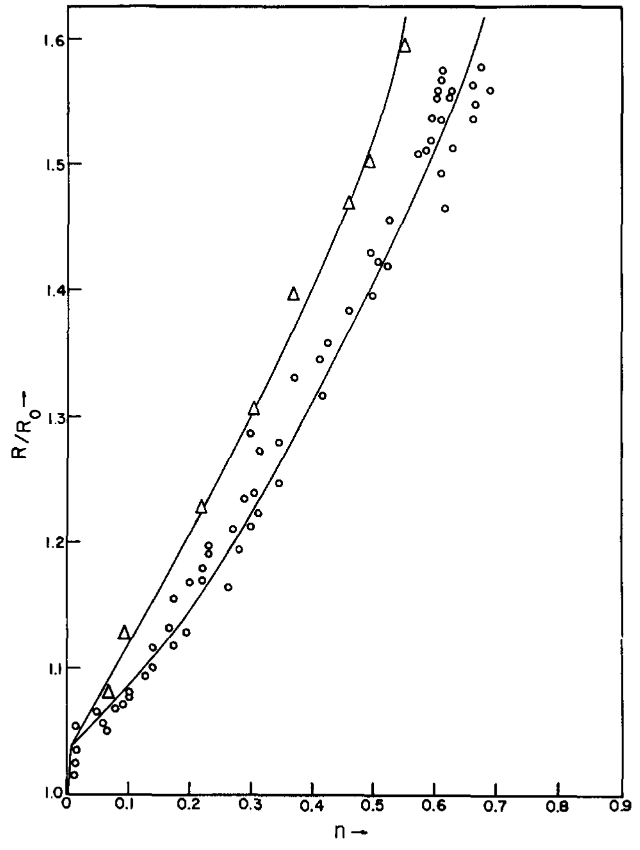

FIG. 3. Typical data for R/R_0 plotted against n (298°K) for a representative alloy ($X_{Cu} = 0.04$) over the entire range of hydrogen contents available up to 1 atm of H_2; ○, Pd/(0.04)Cu alloy; △, Pd (*15*).

of hydrogen upon the electrical resistance must be greater in the α- than in the β-phase. It should be noted that much of the data reflected in Fig. 4 represents regions of coexistence of two phases and therefore the changes of R/R_0 with n are not continuous but reflect only the changing proportions of these two phases. The region of solution of hydrogen in the β-phase commences at the following values of n: 0.58 (Pd), 0.52 ($X_{Cu} = 0.04$), 0.48 ($X_{Cu} = 0.08$), 0.40 ($X_{Cu} = 0.16$), and 0.22 ($X_{Cu} = 0.23$). Above these values of n, the variation of R/R_0 with n is continuous.

The conclusions that can be drawn from these detailed resistance data differ from those of Burch and Buss (*1*). It is concluded that the effect of interstitial hydrogen on R/R_0 decreases with X_{Cu}, that the increase of ρ with interstitial hydrogen is almost constant with X_{Cu}, and that there is a definite change of slope at the lower phase boundary. Both studies show that at hydrogen contents accessible up to 1 atm of hydrogen pressure, maxima or minima are not observed in these relationships such as those that are observed for Pd/Pb (*9*), Pd/Ag (*13*), and Pd/Au (*14*). The Pd/(0.23)Cu alloy shows some tendency to exhibit a maximum (Fig. 4) so it would be anticipated that extrema may exist at larger hydrogen contents.

α-Phase Isotherms and Thermodynamic Parameters at Infinite Dilution

The absorption isotherms at 323°K are shown in Fig. 5. The degree of reproducibility is illustrated for $X_{Cu} = 0.10$ and 0.19. There are three separate absorption isotherms for

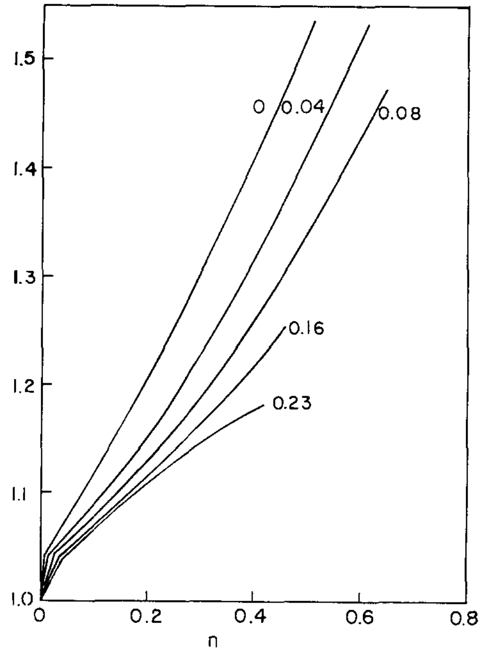

FIG. 4. Relationships of R/R_0 plotted against n over the entire range of hydrogen contents available up to 1 atm of H_2 pressure (298°K). Numbers on curves indicate atom fraction copper.

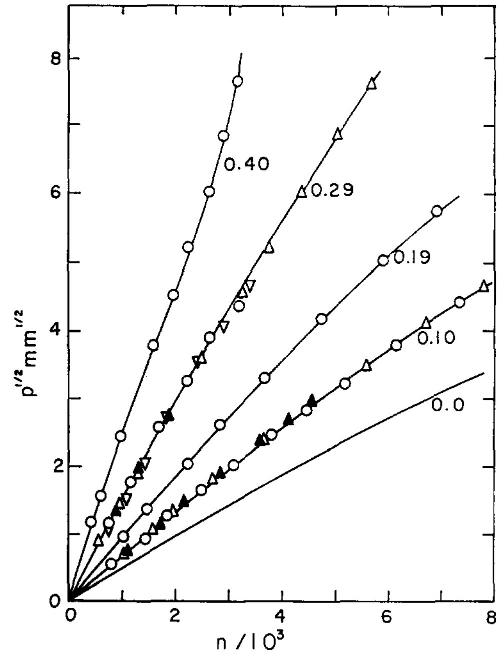

FIG. 5. Absorption isotherms for Pd/Cu alloys in the α-phase region (323°K). △, ▽, and ○, represent repetition of isotherms and ▲ represents determination of an isotherm in a different apparatus.

each of these alloys plus an additional isotherm for each alloy which was determined in an entirely separate vacuum system from the other data. The degree of agreement is seen to be excellent. Similar data have been determined at 273, 303, and 348°K. The temperature range employed here is lower than that used by Burch and Buss (*1*) who studied α-phase solubilities from 423 to 573°K. The solubility is greater in the present study because of the lower temperature range. The present investigation covers copper contents up to $X_{Cu} = 0.40$ whereas the study in (*1*) extended only to $X_{Cu} = 0.20$. Their data (*1*) in the α-phase consists of four equilibrium pressure–hydrogen content data points for each of four temperatures over hydrogen contents from about $n = 0.005$ to 0.020. Their Pd/Cu samples were coated with palladium black in order to promote the equilibrium $H_2 \rightleftarrows 2H$. It has been noted in investigations of the solubility of hydrogen in the α-phase of Pd/Rh alloys (*6*) that a fine deposit of palladium black leads to spurious α-phase data unless the samples are sintered at $\geqslant 673$°K, and even after such a sintering, a small pressure invariant region was noted due to the $\alpha \rightarrow \beta$ transition in the palladium-black coating. This extended typically from $n = 0.014$ to 0.022, where n refers to the alloy mass, not the mass of the fine-coating. The highest equilibrium pressure of their α-phase data (*1*) is just below the expected plateau pressure of pure palladium so that it is not known whether such a spurious plateau was detected in their research. In any case, it is most desirable to avoid a coating of palladium black on palladium alloys when studying the α-phase solubilities. Nonetheless, the general features of the α-phase data are similar in both studies, i.e., the equilibrium hydrogen solubility declines progressively with X_{Cu} in the low hydrogen content region, i.e., the opposite behavior of Pd/Ag (*7*) and Pd/Au (*14*).

Values of $\Delta\bar{G}^{xs}_{H\to o}[= RT\ln p^{\frac{1}{2}}(1-n)/n]$ (Fig. 6) increases with X_{Cu}. From the temperature-dependence of these partial free energies,

TABLE III

RELATIVE PARTIAL THERMODYNAMIC PARAMETERS FOR SOLUTION OF HYDROGEN IN Pd/Cu ALLOYS AT INFINITE DILUTION OF HYDROGEN (273–348°K)

X_{Cu}	$\Delta\bar{H}_{\mathrm{H}\to 0}$(J/g-atm H)	$\Delta\bar{S}^{xs}_{H\to 0}$(J/deg g-atm H)	$\Delta\bar{H}_{\mathrm{H}\to 0}$(J/g-atm H)	$\Delta\bar{S}^{xs}_{H\to 0}$(J/deg g-atm H)
0.00	−9830 (*29*)	−53.5 (*29*)	−9000 (*1*)	−51.0 (*1*)
0.10	−8700 ± 400	−54.8 ± 1.5	−8700 (*1*)	−51.8 (*1*)
0.19	−8500	−55.5	−8000(*1*)	−54.0 (*1*)
0.29	−8300	−59.2	—	—
0.40	−7700	−61.5	—	—

values of $\Delta\bar{H}_{\mathrm{H}\to 0}$ and $\Delta\bar{S}^{xs}_{\mathrm{H}\to 0}$ can be determined and are shown in Table II. These thermodynamic parameters have been determined from the slopes of the absorption isotherms at $n \to 0$ and also from the temperature dependence of the intercepts of plots of $\Delta\bar{G}^{xs}_{\mathrm{H}}$ against n (*17*). The values shown are based on the latter method and the error is estimated from the difference of the two methods. Table III shows that the relative partial enthalpies of absorption are all more positive than for pure palladium but the increase with X_{Cu} is very small. The values are in reasonable agreement with those given by Burch and Buss (*1*). There is a regular decrease in the relative partial excess entropies of absorption with X_{Cu} but it is a significantly smaller decrease than has been noted for the other members of the alloy series. For instance, $\Delta\bar{S}^{xs}_{\mathrm{H}\to 0} = -66.1$ J/deg g-atom H for Pd/(0.30)-Ag (*7*) and −65.3 J/deg g-atom H for Pd/(0.27) Au (*18*). The increase of $\Delta\bar{G}^{xs}_{\mathrm{H}\to 0}$ with X_{Cu} is much more dramatic (Fig. 6) than the increase of the partial enthalpy or the decrease of partial entropy; the latter changes are the major cause of the changes of the partial free energy with X_{Cu}.

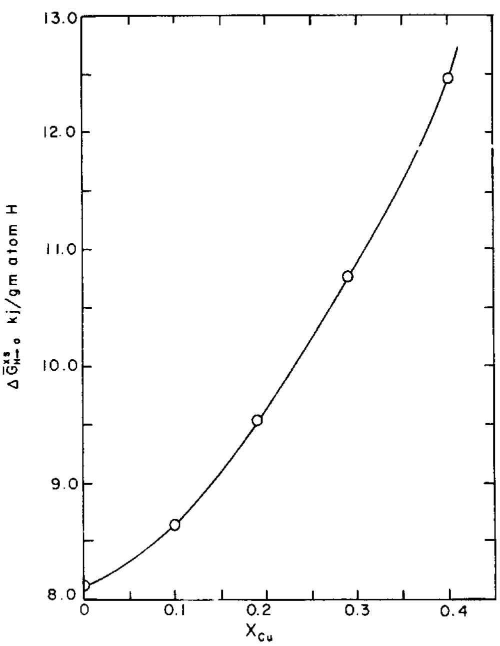

FIG. 6. Plot of $\Delta\bar{G}^{xs}_{\mathrm{H}\to 0}$ against X_{Cu} (323°K).

There have been reports of short-range order in Pd/Cu alloys (*19*). The Pd/(0.35)Cu alloy is in the composition range where such effects have been noted. This alloy was subjected to three different heat treatments: (1) annealed slowly *in vacuo* from 1073°K to room temperature over a several-day period, (2) annealed at 700°K for several days *in vacuo*, (3) quenched rapidly from 1073 to 273°K. After each of these treatments, an absorption isotherm was remeasured (323°K) and there was no difference between the various isotherms. This does not prove the absence of a potential effect of short-range order on the hydrogen solubility in palladium alloys but only that the above heat treatments on this particular alloy did not achieve any differences in the degree of short-range order or else any short-range order differences did not play a role for this specific Pd/Cu alloy. It shows, however, that differences in heat treatments for these alloys are not likely to have any effect on their equilibrium solubility data.

The H–H attractive interaction (or apparent interaction), w, can be evaluated from plots of $\Delta\bar{G}_H^{xs}$ against n (with the assumption that n_s—the limiting hydrogen-to-metal ratio—is 1) (*7–9*, *17*). Typical plots are shown in Fig. 7 (323°K). There is considerable scatter in the values of the slopes between various isotherms at a given temperature but not in the slope determined from a given isotherm, e.g., the regression coefficients for a given set of isothermal data were generally 0.99. The scatter in values of w from different sets of data probably arises from systematic errors, e.g., a trace of hydrogen initially present in the sample from incomplete outgassing. The value of w, the pairwise interaction energy, is obtained from

$$(\partial\Delta\bar{G}_H^{xs}/\partial n)_{p,T} = 12RT(1 - \exp - w/RT) \tag{1}$$

The seemingly identical absorption isotherms shown in Fig. 5 for the Pd/(0.29)Cu alloy (323°K) give values of w ranging from −2786 to −3234 J/g-atom H. Thus a very small error in either n or $p^{\frac{1}{2}}$ affects the slopes significantly. Despite the scatter in the values of w, it is clear that these values are more negative than for palladium itself, i.e., the H/H interaction is increased. For the Pd/(0.40)Cu alloy there is

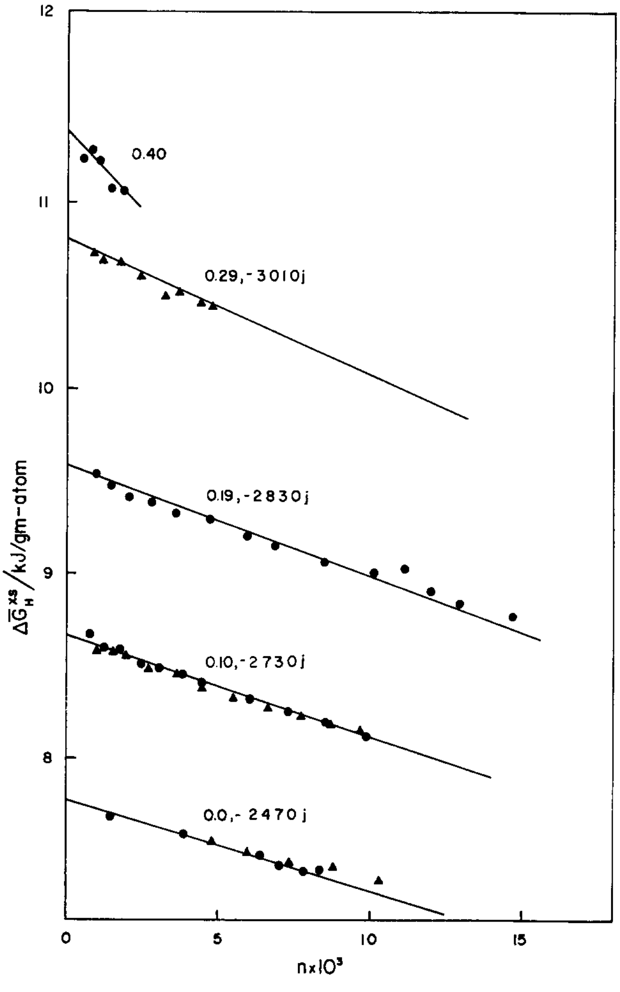

FIG. 7. Plots of $\Delta\bar{G}_H^{xs}[= RT\ln p^{\frac{1}{2}}(1 - n)/n]$ at 323°K. The first numbers on the graphs indicate the atom fraction copper and the second the value of w. The various symbols represent repetitions of the absorption isotherms shown in Fig. 5.

an initial very steep slope followed by a change of slope. This can be connected to the change of slope for the isotherm for this alloy (Fig. 5). Apparently a factor other than the H–H interaction enters at very small values of n for this alloy; similar behavior has been noted for some Pd/Au alloys and has been attributed to the onset of a decreased energy of electron donation (*20*). The interaction energy has also been noted to be greater than for palladium for the other "contracted" alloys such as Pd/Ir (*5*), Pd/V (*21*) and Pd/Rh (*18*). At a given temperature the magnitude of the interaction energy increases slightly with X_{Cu}. It has been found here that the value of w decreases with temperature. This has not been previously reported and, in fact, the opposite trend was given for palladium/H_2, i.e., $w = -3196.6 + 1.083T$ J/g-atom H (*22*). The increase in interaction energy (decrease of w) with temperature has also been noted by one of the present workers in a study of Ag/Pd alloys (*23*). The decrease found here is considerable, i.e., w decreases by about a factor of two in increasing the temperature from 273 to 400°K. Wagner's (*24*) treatment of the thermodynamics of hydrogen absorption predicts the opposite trend, since the compressibility increases with temperature. The observed decrease is apparently limited to alloys, rather than pure palladium, and no explanation can at present be given.

Phase Diagram for Pd/Cu/H

The relationship between Δa_0 $(= a_0(n) - a_0)$ and X_{Cu} is shown in Fig. 1 for hydrogen-containing alloys in their two phase regions (298°K). The value of Δa_0 is expected to be closely proportional to n (*25*). Data are also shown for the phase boundaries as determined by Burch and Buss (*1*) from their absorption isotherms; their data are for 303°K rather than 298°K but this small change should make no difference in the predicted phase compositions. It can be seen that their phase diagram is more symmetrical than that determined from X-ray measurements of the lattice parameters. In the present research the lower α/β phase boundaries have also been estimated from absorption isotherms carried to larger values of n than shown in Fig. 5. In addition, these boundaries can be estimated from the values of n where the R/R_0 relationships change slope (298°K, Fig. 4). The upper phase boundaries agree well with the previous estimate (*1*) but the lower boundaries do not. The three different approaches employed here for the determination of the lower boundaries are in good agreement and the result is a more unsymmetrical isotherm than previously given (*1*). It is not unexpected that the low phase boundary would occur at lower values of n in Pd/Cu than for the other Pd/group IB alloys because of the larger negative H–H interaction for the Pd/Cu alloys. Two-phase formation persists in this system to large values of X_{Cu} because $\Delta \bar{H}_{H\to 0}$ is not very different from palladium, $\Delta \bar{S}^{xs}_{H\to 0}$ does not decrease markedly with X_{Cu}, w is quite negative, and there must be no adverse electronic factors at large n values.

These data on the Pd/Cu system allow the intercomparison of the Pd/group IB alloys in some detail. This system behaves quite differently (under zero effective pressure conditions) from the other two members of these alloy series. An uncontrollable experimental variable in these comparisons is the molar volume of the alloy, which is smaller at a given value of X_M for Pd/Cu than for the other two alloys. The compressibility of copper lies between that of silver and gold and therefore its role is not expected to be a determining one in its different behavior. For Pd/Pt alloys the values of $\Delta \bar{H}_{H\to 0}$ increase markedly with X_{Pt} (*18*) despite the expansion of the lattice upon substitution of platinum. This suggests that Pd/Cu alloys are much more favorable electronically for hydrogen absorption than are Pd/Pt alloys, despite the partially filled d bands in platinum itself. The evidence cited from studies of superconductivity of Pd/Cu alloys (*10*), suggests that even for a very copper-rich alloy, i.e., Pd/(0.85)Cu, large amounts of hydrogen can be dissolved—the charging of hydrogen in these superconductivity studies is done by ion implantation. Furthermore, CuH has been prepared (*26*) (it has a wurtzite structure). Neither silver nor gold hydrides have been prepared. This lends support to the greater bonding of interstitial hydrogen in Pd/Cu as compared to Pd/Ag or Pd/Au alloys.

Ganguly (*27*) has suggested that the variation of the position of the maximum superconductive transition temperature, T_c, with X_M arises from a disorder–order transformation in the binary alloy matrix. The values of X_M at which the maximum values of T_c appear are: 0.15, 0.30, and 0.45, for gold, silver, and copper/palladium alloys, respectively (*10*). Ganguly proposes that the disorder–order transformation appears at slightly higher values of X_M for each of these alloys and this causes the superconduction (and cessation of β-phase formation) to decline. It is suggested here instead that a large solubility of hydrogen persists to larger values of X_M in the increasing sequence: Pd/Au, Pd/Ag, and Pd/Cu. One reason why this sequence is proposed is because it has been found in the present work that absolute values of $(\partial \Delta \bar{S}^{xs}_{H\to 0}/\partial X_M)_{T,P}$ decrease in the sequence: Pd/Au, Pd/Ag, and Pd/Cu. Although this is an entropy term, it relates to the energetics of absorption of hydrogen indirectly because interstices are effectively excluded for occupation on energetic grounds and to a greater extent in Pd/Au than in Pd/Ag, and in Pd/Ag than in Pd/Cu.

Oates and Flanagan (*28*) have recently extended Wagner's formulation (*24*) in order to show that values of $\Delta \bar{G}^{xs}_{H\to 0}$ under constant volume conditions (that of the molar volume of pure palladium) are different from the measured values of $\Delta \bar{G}^{xs}_{H\to 0}$ (at zero effective pressure). Thus it is predicted that Pd/Cu alloys would absorb hydrogen more readily than either Pd/Ag or Pd/Au alloys under conditions of constant alloy volume. Most of this difference of behavior must be attributed to differences to the energetics of absorption. High pressure studies of the Pd/Cu/H system would be of great interest and it is not unlikely under high pressure conditions that copper will absorb hydrogen when within the palladium matrix.

Acknowledgments

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