The solubility of oxygen in Pd from its subsequent trapping of hydrogen

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Abstract

Solubilities of O in Pd have been measured by exposing Pd to O_2 (g) at elevated temperatures, 1073–1223 K, for sufficient times to obtain equilibrium. The amounts of dissolved O are determined from the extent of subsequent trapping of H by O (323 K). The solubility enthalpy is -49 ± 4 kJ/mol $\frac{1}{2}O_2$.
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1. Introduction

Bulk Pd is known to oxidize in air from about 475–1090 K [1–4] with the oxidation confined to the surface and near surface regions; at >1090 K the oxide becomes unstable in air and decomposes to Pd.

Pd also dissolves a small amount of O at elevated temperatures; two sets of solubility data [5,6] are in reasonably good agreement at 1123 K whereas others differ markedly, e.g., [7]. In the present research O_2 solubilities will be determined from measurements of H solubilities in Pd containing dissolved O. The H is trapped by the dissolved O and the amounts can be determined from the intercepts along the H/Pd axis of the H_2 solubility plots of $P_{H2}^{1/2}$ against r, where $r = $ H/Pd,

atom ratio. The oxygen solubilities will be determined from the amount of trapped H and the number of H atoms trapped per dissolved O atom; the latter will be determined by comparison with O_2 solubilities measured elsewhere with different techniques [5,6]. H is known to be trapped by bcc metals such as Nb containing dissolved O, and one H is trapped per dissolved O [8,9].

2. Experimental

Pd (99.9% purity) foils (90–150 μ) were prepared by arc-melting, rolling and annealing (1133 K). After most determinations, in order to ensure that the dissolved O and H were completely removed and, to remove any effects if the specimen had been hydrided, the foils were remelted, rolled and annealed. In order to dissolve O the Pd foils were exposed to O_2 (g) at 0.101 MPa for the desired times at temperatures between 1073 and 1223 K and then quenched into water. After

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equilibration with O_2 at these temperatures, the Pd foils were exposed to He(g) at about 1053 K for 20 min to decompose any PdO which had formed near the surface.

H_2 solubilities were determined volumetrically in a Sieverts' type apparatus. The trapped H is determined from the extent of an initial region where the traps are being filled where $P_{H_2} \approx 0$. After these traps are filled, there is an abrupt transition to the dilute solubility region where P_{H_2} becomes measureable.

3. Results and discussion

3.1. Determination of the amounts of dissolved O in palladium

Equilibrium solubilities at $P_{O_2} = 0.101$ MPa were obtained after exposure to O_2 for times deemed to be sufficient for equilibrium. For example, after 48 h equilibration at 1123 K a saturation solubility of O was obtained because the solubility after 24 h was almost the same.

Fig. 1 shows that the H_2 solubility (323 K) in annealed Pd intersects the origin, i.e., follows the law of ideal dilute solubility as $r = (H/Pd) \rightarrow 0$. The H_2 solubility for Pd-containing O deviates from ideal dilute solubility behavior because there is a region where $P_{H_2} \approx 0$ before it increases at the onset of H_2 solution in the dilute phase (Fig. 1).
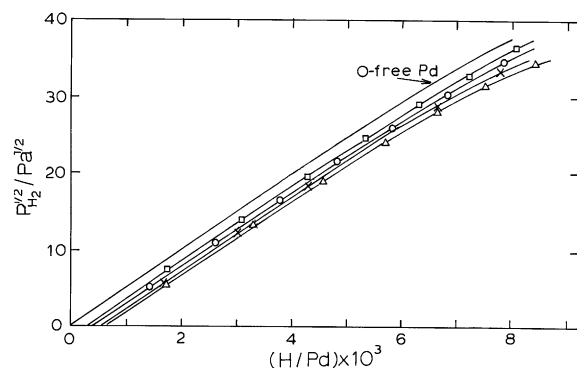
The extent of the regions where $P_{H_2} \approx 0$ corresponds to the amount of trapping by dissolved O.

From the equilibrium solubilities reported by Jehn and Grallath [5] at 1123 K and $P_{O_2} = 0.101$ MPa, (O/Pd) = 0.00066 or 0.066 at.% which is somewhat larger than the value of 0.056 at.% obtained by extrapolation of Gegner's data [6]. The latter is closer to the present values of 0.052–0.053 at.% assuming that one H atom is trapped by one dissolved O atom and therefore one O atom traps one H atom since it is unlikely that less than one H per O. Although there are several examples of bcc metals such as Nb or Ta where dissolved O traps H [8,9], this investigation shows that dissolved O in an fcc metal also traps H.

The oxygen solubilities decrease with increase of temperature of equilibration with O_2 indicating that the solubility reaction is exothermic as proposed by some recent studies [5,6] but not in earlier studies [10–12] and not by Park and Altstetter [7].

Jehn and Grallath [5] derived from their solubility data, $\Delta H^\circ = -17.6$ kJ/mol and $\Delta S^\circ = -76.5$ J/K mol for the solution of $\frac{1}{2}O_2$ (0.101 MPa, ≈ 1330 K). The dissolved O was determined by extraction after equilibration at temperatures from 1148 to 1573 K. There is, however, considerable scatter in their data.

Fig. 2 shows a plot of $\log X_o$ against $1/T$ from the intercepts in Fig. 1, $\Delta H^\circ = -49 \pm 4$ kJ/mol and $\Delta S^\circ = -107 \pm 15$ J/K mol where X_o is the

Fig. 1. The equilibrium solubilities (323 K) of H_2 in Pd after exposure to O_2 at 0.101 MPa. □, 1223 K (22 h); ○, 1173 K (36 h); ×, 1123 K (48 h) and △, 1073 K (96 h).
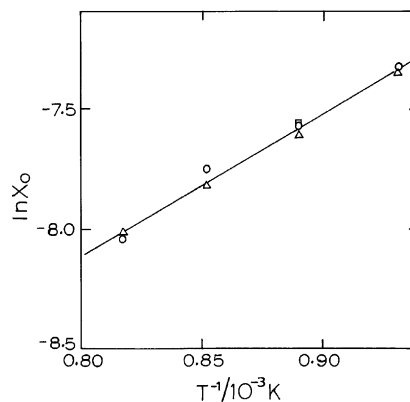

Fig. 2. A plot of the solubilities of dissolved O in atom fraction $O(X_o)$ against $1/T$. The different symbols at each temperature represent determinations using different Pd samples.

atom fraction of O. The solubility measurements at 1073 and 1123 K were repeated with newly oxygen-charged Pd samples three times and the other temperatures twice (Table 1). The error is due to the small interval of $1/T$ and to the difficulty in locating the intercepts precisely. These thermodynamic parameters differ considerably from those given by Jehn and Grallath [5].

In one experiment the O_2 solubility was determined at 1073 K and then the same Pd sample was exposed to O_2 at 1223 K for sufficient time to obtain a new equilibrium. Its O solubility was then re-determined at 1223 K from the extent of H trapping and it agreed very well with the solubility determined for the Pd which had been melted and re-annealed before the determination. In the sample which initially contained O–H pairs from equilibration at 1073 K, some O and trapped H must have been lost in order to re-equilibrate with O_2 at 1223 K. These results demonstrate that equilibrium must have been established in both of these experiments.

The O_2 solubilities at 1023 K were determined at $P_{O_2} = 20$ kPa and at 100 kPa. The results are as anticipated for a dependence of the solubility on $P_{O_2}^{1/2}$, i.e., the solubility at 100 kPa was $2.1 \pm 0.2 \times$ greater than at 20 kPa which is very close to the expected ratio of 2.2.

3.2. The removal of trapped H by heating/evacuation

Pd was exposed to O_2 at 1123 K for 20 h (0.101 MPa) and subsequently H_2 was absorbed (323 K) to determine the O trap population. The Pd was then evacuated at a series of increasing temperatures and, after each evacuation, H_2 was carefully re-absorbed to determine the amount of dissolved O from the H trapping. If some H had been removed from the traps during evacuation, this will be evident by its re-trapping by O during the subsequent H_2 absorption. These results show that trapped H is not removed after 2 h evacuations at either 573 or 673 K. After evacuation at 773 K (2 h) about 30% of the H is removed and after evacuation for 12 h, all of it is removed but the O is *not* because the newly trapped H is almost the same as before these heat/evacuation treatments. This demonstrates that the H is rather strongly bonded to the O but can, nonetheless, be removed under conditions where the O is not removed. The diffusion of O is too slow to leave the Pd at the temperatures in question.

4. Conclusions

The main conclusion is that one dissolved O atom in Pd traps one H atom. This provides a convenient means to determine the O solubilities. The trapped H cannot be removed by evacuation until $T \geqslant 773$ K indicating that the H is rather strongly held by the O. ΔH° for the solution of $\frac{1}{2}O_2$ (g) is -49 ± 4 kJ/mol O which is more exothermic than determined elsewhere perhaps because the experimental method employed earlier [5] was not so accurate for such small solubilities.

Acknowledgement

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Table 1
Oxygen solubilities in Pd, X_o, atom fraction, at 0.101 MPa where each value is an average of two or more determinations

T (K)	X_o
1073	0.00065 ± 0.00001
1123	0.00052
1173	0.00042
1223	0.00032

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