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Summary Report to LANL (Nov. 1996)

Tasks on

Pressure-Composition-Isotherms of

Palladium Alloys.

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Introduction

About one year ago a summary report was submitted covering the previous three years of the contract. This earlier report should be consulted as a useful survey and evaluation of the research carried out by us. Because of difficulties during the current contract period arising from the anomalous nature of the melt-spun alloys received from LANL, it is not possible to contribute much beyond that given in last year's summary with regard to the overall picture of the behavior of Pd-rich alloys towards hydrogen and its isotopes.

In this contract year deuterium was employed instead of hydrogen and instead of using "cycled" alloys, the alloys employed for each isotherm measurement were in their virgin condition. Because of the anomalous behavior of the melt-spun alloys, it was not feasible or worthwhile in some cases, e.g., when the alloy behaved anomalously, to carry out all of the originally proposed work. Nonetheless considering these obstacles, some useful data were obtained. For example, the obtaining of deuterium isotherms for the Pd-Rh alloys down to -40°C using internally oxidized melt-spun alloys may be prove to be useful.

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A Case History of the Anomalous Behavior of Several Melt-Spun Forms of Pd and Pd-rich Alloys.

First it is useful to remind the reader that hydrogen (deuterium, tritium) isotherms for a given metal or alloy, such as Pd, are a fundamental property of a defect(essentially)-free metal or alloy. These isotherms are fundamental relationships between the hydrogen chemical potential and the H content. Thermodynamic properties can be derived from such equilibrium data. When non-negligible defect concentrations are introduced into the metal or alloy, the isotherms are affected and will deviate from the expected, i.e., normal, isotherms because of H-defect interactions [1].

Pure Pd. There are no doubts about the correct isotherms for bulk, low defect Pd-H(D) because these have been measured by many laboratories. The dilute phase solubility and the desorption plateau are especially reliable guides and these have been found to be in good agreement for Pd-H. A bulk, foil sample supplied by LANL, which had been annealed at 1100°C, agreed quite well with these earlier data. Thus any deviations of solubility from that of bulk, low defect (normal) Pd must be regarded as anomalous solubility behavior attributable to some type of defect.

A melt-spun Pd sample was received from LANL last year (Feb. 1995); it will be called MS1. An isotherm for this MS1 Pd differed slightly from one for "normal" bulk Pd, e.g., the 1100°C annealed foil received from LANL. The dilute phase solubility for MS1 was greater at a given p_{H_2} , its plateau pressures were lower and its capacity was smaller than that for "normal" Pd. These differences, however, were not very large and conceivably could have been due to experimental error in the isotherm measurements. This does not seem likely, however, in view of the fact that the anomalous behavior was removed by annealing at an elevated temperature, 860°C, as indicated by re-measurement of the isotherm in the same apparatus. It is concluded therefore that there is a difference between the "normal" bulk Pd and the MS1 Pd but the differences are not very great.

A further sample of melt-spun Pd was received in April of 1996 (MS2) and this behaved more anomalously than MS1. The deviations of MS2 from the "normal" behavior were similar to those for MS1 but larger. Thus the capacity was reduced more dramatically (Fig. 1),

the dilute phase solubility was greater and the plateau pressures were lower than for MS1. It seems clear that the more rapidly cooled Pd has a greater defect concentration than the more slowly cooled, MS1, since the deviations of the isotherm of MS2 from normal, bulk Pd are greater. Annealing MS2 at 860°C caused the anomalous behavior to disappear whereupon the solubility behavior became very similar to normal, bulk Pd (Fig. 1).

It is clear that defects are introduced into MS form of Pd but their nature is, at the moment, uncertain. A possible scenario is that somehow the rapid solidification introduces stress into the Pd which affects the hydrogen solubility. The term defect would then be used in a broad sense to refer to any changes from the essentially perfect, stress-free lattice. Stress can be introduced, for example, by dislocation arrays although this is unlikely for MS Pd.

Pd_{0.90}Rh_{0.05}Co_{0.05}. A case history of a MS ternary alloy will now be described since two MS forms of this alloy have been investigated. One MS alloy was received Jan 1995 (MS1, 90 μ m) and the other in April 1995 (MS2, 30 μ m). The isotherms for these two MS alloys have been shown in earlier (10th report (1995) to LANL, Fig. 14). In addition, the ternary alloy was available in the form of annealed foil from a preparation in our laboratory. The dilute phase data for these MS alloys are shown in Figure 2 and these data show that the hydrogen solubilities at a given pressure are in the sequence: $p_{MS2} > p_{MS1} > p_{anneal}$. The difference between the latter two forms is very small but discernable. The difference between these two forms is hardly discernable for the complete isotherms (Fig. 3). When MS2 was annealed at progressively higher temperatures up to 800°, the solubility did not move towards that of annealed foil (Fig. 2). This contrasts with the behavior of MS2 Pd but agrees with the behavior of the Pd-Rh alloys (Report #4 1996). This suggests that for this MS2 ternary alloy the defect may be an impurity.

Van't Hoff Plots for Pd, and Pd_{0.95}Rh_{0.05}/Al₂O₃.

Van't Hoff plots for the MS2 Pd-Rh alloys after internal oxidation, which contain some unknown, oxide (presumably) were shown in the last report, e.g., Fig. 4. The unknown oxide will not affect the plateau pressures because the matrix becomes essentially pure following internal oxidation. These

plots are for deuterium and were measured down to -40°C . These data should be useful for LANL because I am unaware of equilibrium data for these alloys at such low temperatures especially in view of the fact that the complete isotherms have now been measured including the desorption data. We reproduce Figure 4 from the earlier report but now includes data for Pd-D_2 for comparison. This new plot shows that the van't Hoff plots for these two systems do not cross and therefore the plateau pressures of the $\text{Pd}_{0.95}\text{Rh}_{0.05}$ alloy should always be greater than those for Pd.

Isotherms for Ternary Pd-based Alloys.

These alloys appear to be of some interest because they allow greater flexibility with respect to "tailor-making" plateau pressures and capacities than binary alloys. Some data for ternary alloys are now available from our research and the research of others, e.g., [2, 3, 4]. Unfortunately, due to the anomalous behavior of the recently received MS alloys from LANL, not very much new useful data were obtained for ternary alloys during the past contract period. Judging from the one isotherm measured for the MS $\text{Pd}_{0.90}\text{Ni}_{0.05}\text{Cu}_{0.05}$ alloy, this system may be of some interest because its plateau pressures are considerably greater than those for the $\text{Pd}_{0.95}\text{Rh}_{0.05}$ alloy. The amounts of Ni and Cu could probably be reduced thereby increasing the capacity while still maintaining the plateau pressures at acceptable levels. It may be worthwhile to determine how this Rh-free alloy ages with tritium and, in any case, if its isotherms are acceptable, it would be considerably cheaper than alloys containing Rh.

Conclusions and Recommendations for Further Research.

The ternary $\text{Pd}_{0.90}\text{Ni}_{0.05}\text{Cu}_{0.05}$ alloy described above might be of some interest for the reasons indicated. Isotherms should then be measured for different compositions of the Pd-Rh-Cu system.

Other ternary alloys should be examined such as those having the compositions of the MS alloys received from LANL (April 1996); the alloy sample preparations to be re-examined should, of course, not behave anomalously.

With regard to the overall project it seems to me that there are many important questions that have never been adequately addressed such as do melt-spun, bulk foil, and other forms of the alloys behave similarly with respect to storage? what is the relative importance of alloy homogeneity

with regard to plateau sloping and aging? It seems to me that the fundamental aspects of this research have not been explored completely enough for sufficient understanding of the alloy behavior towards hydrogen. Rather than simply measuring isotherms of different alloy compositions as we have done, it seems that some research should be directed to the fundamental problems; this could ultimately save time and effort.

References

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- [3] F. El-Sanabary, S. Ramaprabhu, A. Weiss, *Ber. Bunsenges. Phys. Chem.*, **97** (1993) 607.
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Figure Captions

- Fig. 1.** Hydrogen isotherms for various forms of pure Pd (50°C). The dashed line is for MS2 Pd; the short dashed line for MS1 Pd; and the continuous line for Pd, annealed at 1100°C. The open symbols are absorption and the full symbols are desorption plateau pressures.
- Fig. 2.** Dilute phase hydrogen isotherms for the Pd_{0.90}Ni_{0.05}Cu_{0.05} alloy at 50°C. The solubilities are shown for the MS1, MS2 and well-annealed alloy forms. Some results after annealing at various temperatures are also shown.
- Fig. 3.** Hydrogen isotherms for the various forms of the Pd_{0.90}Ni_{0.05}Cu_{0.05} alloy (50°C). Isotherms for the Pd/Co (5.2 wt%) alloy at 30°. The open symbols are absorption and the full symbols are desorption plateau pressures.
- Fig. 4.** Van't Hoff plots (deuterium) for Pd_{0.95}Rh_{0.05}/MO_x, Pd_{0.95}Rh_{0.05}/Al₂O₃ and for Pd/Al₂O₃. The open symbols are absorption and the full symbols are desorption plateau pressures.

$$P_{H_2}'' / \text{torr}^{1/2}$$

Fig 2

Fig. 3

1. H_2 , nicht-sauer H_2S - I
 2. O_2 , mild sauer H_2S - II
 3. H_2O_2 , amnestet Fäul-
 mangel H_2S -

$Pd_{0.95}Rh_{0.05}$

$T =$

Fig. 4

N-S-T oxidized

at 1000°C

$\circ$ $\bullet$ Al₂O₃ oxidized
 $\circ$ $\bullet$ oxidized Pd/Rh
 foil

	$\Delta H_{plat}/KJ/mol$	$\Delta S_{plat}/J/K/mol$
abs	-15.7	-49.9
des	+17.2	50.8
AVI	16.5	50.7

$\circ$ $\bullet$ Pd/Al₂O₃

$\frac{1}{2}$
 $\rightarrow$ 1.3 [Pd]