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The Effect of Alloy Microstructure on the Behavior of Pd and Pd-based Alloy towards H_2

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Abstract

The influence of different microstructures and compositional variations on hydrogen absorption by pure Pd, and $Pd_{0.9}Rh_{0.1}$ alloy has been examined from changes in the hydrogen isotherms. The dilute phase solubilities and the plateau pressures are affected by differences in microstructures and compositional variations but the hydrogen capacities at relatively high hydrogen pressures are not affected except for the alloy form which has some phase separation.

1. Introduction

The behavior of Pd-rich alloys towards $H_2(g)$ has been a subject of investigation for well over 100 years resulting in a voluminous literature. In these publications little attention has been paid to how the hydrogen solubilities are affected by the metallurgical state of the alloy, i.e., on its microstructure which will include compositional variations in this paper. In papers on hydrogen solubilities there is often no statements concerning the pre-treatment of the alloy. In this paper the effect of the microstructure on the hydrogen absorption behavior will be examined experimentally employing $Pd_{0.9}Rh_{0.1}$ alloy. This alloy are not representative of Pd-rich alloys because it is metastable with respect to phase separation [1, 2] and it therefore has a tendency to segregate. In this paper, the effect of quenching rates on the behavior of some Pd-Rh alloys towards hydrogen will be discussed, and the effects of microstructure on the isotherms will be examined. Differences between the roles of microstructure on the hydrogen absorption behavior of these alloys and pure Pd will be discussed. The proposition that the microstructure affects the hydrogen solubility of an alloy can be turned around and it can be asked how hydrogen solubility can be employed to probe the microstructure of an alloy in this work.

2. Experimental

The palladium employed is in the form of thin foil of thickness $140 \pm 10\,\mu m$. It was used for isotherm determinations after abrading with fine emery paper and cleaning ultrasonically with acetone. An all-metal Sieverts-type apparatus was employed for isotherm measurements; corrections being made for the non-ideality of $H_2(g)$ and the volume expansion of the metal with hydrogen.

The starting $Pd_{0.9}Rh_{0.1}$ alloy was prepared by arc-melting the pure metals under argon. The alloy was annealed for 3 days at 1123 K, rolled into thin foil and re-annealed under the same conditions. Another alloy of the same nominal composition was obtained from the University of Vermont, US. An annealed form of the alloy refers to one prepared in this way and then after annealing it at 1123 K, it was cooled at the rate of 150℃ per hour in the furnace. Most forms of the alloy employed were thin foil of ~140 ㎛ thickness except for spin cast forms. The spin cast form was in the foil, about 80㎛ thickness.

The average alloy composition for $Pd_{0.9}Rh_{0.1}$ was determined by electron microprobe analysis to be 10.0at% of Rh, however, in some cases, concentration fluctuations appeared across the alloy, the magnitude of which depended on the pre-treatment, i.e., the form of the alloy.

Slowly quenched refers to the form of the alloy which was initially in the annealed condition described above and then heated in the atmosphere to red heat in a flame and then quickly cooled in air. Because Pd and Rh are precious metals, this procedure, while seemingly crude, is effective and does not lead to significant oxidation. Rapidly quenched refers to the same procedure except that, instead of cooling in air after the heating in a flame, the foil is rapidly quenched into an ice bath. Both procedures gave reproducible results and, as will be seen below, the solubility results for the rapidly quenched and the spin-cast forms are quite similar attesting to the effectiveness of the former method.

The spin-cast form of the alloy was obtained from the University of Vermont, US and was used without further pre-treatment. It was in the form of foil of ~80㎛ thickness. This alloy was analyzed by electron microprobe analysis and its composition was 10.4±0.1 at% Rh; where the composition fluctuations across the foil are indicated by the 0.1at% and do not exceed this.

The alloy form referred to as phase-separated has been exposed to $H_2(g)$ at an elevated temperature and pressure; the details of its preparation will be described in results and discussion.

The isotherm measurements were carried at 323 K for alloys studied. The cycling involved hydriding and dehydriding at 323 K. The alloys were not heated above this temperature in order to avoid any effects of annealing, i.e., so that all of the effects arose from the cycling.

3. Results and Discussion

Schematic isotherm for a metal-hydrogen system would appear as illustrated by Figure 1. Starting from the origin(A), the hydrogen pressure in the dilute phase is related to the hydrogen content by the law of ideal dilute solubility for a dissociating gas, i.e. $(H/M) = r = K_s \times P^{1/2}$, Sieverts' law. At higher hydrogen contents, an H-H attractive interaction leads to increasing deviations from Sieverts' law and to the eventual appearance of the hydride phase at the concentration referred to as the terminal solubility of hydrogen (B, Fig. 1). At the terminal solubility of hydrogen two solid phases commence to co-exist with the gaseous phase, H_2 and upon further addition of hydrogen, as the dilute, α-phase, is converted to the hydride phase, β, the hydrogen pressure must be invariant according to the phase rule. This invariant pressure is referred to as the plateau pressure. At point C all of the dilute phase has been converted to the hydride phase and the pressure, which is related to the hydrogen chemical potential, then increases with the hydrogen content, C-D, in the single hydride phase, β.

3.1 Isotherms for Pure Pd-H

Needless to say, the Pd-H system has

been studied many times. The purpose of the present investigation was the examination of the effect of repeated cycling through the hydride phase transition. Its ''cycling'' behavior will then be compared with that of the alloy which will be described below. Results of the dilute phase are shown (323 K) in Fig. 2 and for the complete isotherm in Fig. 3. It can be seen that the largest solubility enhancement occurs after the first cycle and thereafter there is a further small increase and no difference is observed between the seventh and the twenty second cycle. The Pd sample was then annealed at 693 K for 12h after twenty second cycle and the solubility enhancement disappeared completely. A supersaturation of the α-phase is observed, as has been previously observed [3]. But this is observed only in the annealed alloy and not for subsequent cycles. It is of interest that this supersaturation was not observed for any of the several forms of Pd-based alloys. The supersaturation is caused by the difficulty of nucleation of the hydride phase.

The effect of cycling on the plateau is shown in Fig. 3. After annealing the initial hydriding shows a supersaturation effect. For the second cycle a very small increase of the absorption plateau, P_f, occurs, but there is no effect on the desorption plateau, P_d. After 9 cycles there is a significant increase in P_f and a small decrease of P_d. After 21 cycles the changes are about the same as 10 cycles. After annealing for 12 h at 693 K, the plateau, as also observed for the dilute phase, is completely restored to its initial condition. Earlier studies of the effects of cycling [4] were limited to three cycles where the solubility enhancement appeared to level off. Thus this work confirms the earlier study.

With reference to the hydrogen-treated alloy (see below in Fig. 7) which results in phase separation according to the phase diagram, a Pd sample was subjected to similar conditions and there was no change in its subsequent isotherm measured at a low temperature, 323 K. This indicates that the change introduced by the hydrogen are related to the multicomponent character of the sample, i. e., the $Pd_{0.9}Rh_{0.1}$ alloy.

3.2 Isotherms for various forms of $Pd_{0.9}Rh_{0.1}$

Isotherms for various forms of the same composition, $Pd_{0.9}Rh_{0.1}$, have been measured at 323 K. For each form of the alloys the effect of repeated hydriding and dehydriding, it is called "cycling", of the alloy have been examined. The various forms of the alloy whose isotherms are to be compared are: spin-cast, rapidly quenched, slowly quenched, annealed and the phase separated form of the alloy which has been subjected to a hydrogen treatment at moderately high hydrogen pressures and temperature which results in some phase separation according to the phase diagram [1, 2].

3.2.1 The Spin-cast, Rapidly Quenched, Slowly Quenched and Annealed Forms.

These alloy forms are grouped together because they are often, except for the spin-cast one, considered to be equivalent from the viewpoint of their hydrogen absorption behavior. But, for the present study, it was found that differences of hydrogen solubility behavior of these forms of the alloy obtain for both the dilute and two phase regions as illustrated in Fig. 4, 5 and 6.

Dilute Phase Solubilities

The isotherms for the dilute phase for these forms of the alloy are shown in Figure 4. As pointed out before [5], the rapidly quenched and spin-cast forms have identical isotherms, i.e., both exhibit sharp phase transitions to the hydride phase during the first cycle of hydriding but no supersaturation effects in contrast to pure Pd, which is surprising. The slowly quenched one has a greater solubility than the rapidly quenched one over the whole of the dilute phase region with a relatively sharp transition to the hydride phase. The annealed form has a similar sharp as the slowly quenched one but there is a somewhat greater solubility at each pressure in the dilute phase. The preparation method of the annealed form is one which is routinely used to prepare Pd-rich alloy and, as seen here for the present alloy, it leads to a microstructure which causes its isotherms to significantly differ from that for the spin-cast or rapidly quenched forms.

In the second cycle of hydride formation and decomposition for each of these alloy forms there is an enhanced dilute phase solubility with a more rounded transition to the hydride phase which is similar to pure Pd-H[4] and is attributed to hydrogen segregation to dislocations and especially to microstresses which allow the hydride phase to form before the normal transformation pressure is reached.

Complete Isotherms

For these various alloy forms the absorption plateau branches differ from each other more than do the desorption branches for the complete, initial isotherms, as shown in Fig. 5. The plateau pressures(P_f) of the initial isotherms for hydride formation are in the order: spin-cast = rapidly quenched > slowly quenched > annealed and the decomposition plateau pressures(P_d) are in the order: slowly quenched = spin-cast > rapidly quenched = annealed. The differences in the P_d values may not be of significance since they are close. The hydrogen capacities of all the alloy forms are the same to within experimental error, however, the shapes of the desorption isotherms in the β-phase region differ. The spin-cast and rapidly quenched forms show a more sharper transition from the hydride phase to the two phase region

than the slowly quenched or annealed forms as shown in the figure.

The rapidly quenched or spin-cast forms have almost identical isotherms as shown in Fig. 5 and it will be assumed that microstructure plays a minimal role for the initial cycle of hydriding and dehydriding of this polycrystalline material. These forms will be referred to as reference materials with the corresponding reference isotherms for the polycrystalline alloy. After the first cycle, of course, defects are introduced into these forms from the phase change.

Repeatedly cycling of the initially spin-cast alloy form leads to the behavior shown in Fig. 6 where it can be seen that, in contrast to pure Pd (Fig.3), the plateau pressure for hydride formation decreases with cycling. With increase cycling the plateau for hydride formation becomes more sloping. The transition from the two phase region to the hydride phase becomes more around and the transition during decomposition from the two phase region to the dilute phase also becomes around with cycling, i.e., the effect is a symmetrical one. Its origin should be related with defect, dislocations [6, 7, 8, 9].

3.2.2 The Phase Separated Form

Fig. 7 shows the effect of phase separation on the plateau regions, and it shows significantly different hydrogen solubilities in result from phase separation. The solubility enhancement of the H-treated, phase separated form is appreciable and is due to the formation of a Pd-rich phase which absorbs more hydrogen at a given pressure in the dilute phase than does the reference homogeneous alloy. With different hydrogen heat treatment, large differences in isotherms are found. The plateau pressure for hydride formation decreases continuously with increase time of heat treatment. This dependence of the plateau pressure values upon exposure times of the heat treatment may result from the phase segregation according to the phase diagram. There is also seen to be a significant effect leading to a shortening of the plateau. This is caused by the phase separation into Pd-rich and Rh-rich phases. At the hydrogen pressures employed for the measurement of the diagnostic isotherms (Fig. 7), the former will absorb hydrogen and the latter will not. One purpose in showing these isotherms for these examples of rather extreme phase separation is because some antecedents of this behavior are seen in the behavior of the annealed and slowly quenched forms. The annealed form shows a lower P_f and a slightly lower capacity (Fig. 5) than the reference one which is in the direction of the changes seen in the phase separated form of the alloy (Fig. 7).

4. Conclusions

It has been shown that significantly different hydrogen solubilities are observed for different forms of the same

alloy. The dilute phase solubilities and the plateau pressures are affected by differences in microstructures and compositional variations but the hydrogen capacities at relatively high hydrogen pressures are not affected except for the alloy form which has some phase separation. This particular alloy, $Pd_{0.9}Rh_{0.1}$, is metastable with respect to separation into Pd-rich and Rh-rich phases so that it is somewhat exceptional but, nonetheless, other Pd-rich alloys may, also show differences of solubility depending upon the forms of the alloy. In addition, some Pd-rich alloys may exhibit hitherto unknown phase separation or ordering under the influence of hydrogen, e.g., Pd-Pt [10].

Acknowledgement

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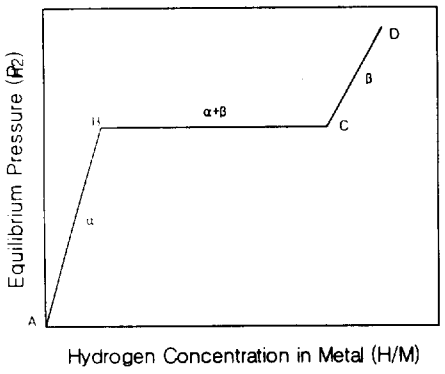

Fig. 1. Schematic isotherm for a metal-hydrogen system which forms a hydride phase but with no effects arising from hysteresis and alloy microstructure.

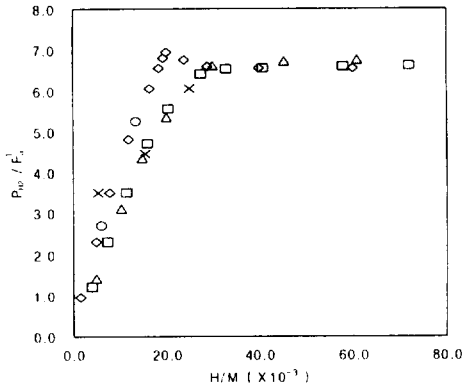

Fig. 2. Dilute phase solubility for Pd-H at 323 K. ◇, after annealing where a supersaturation effect can be seen; □, second cycle after complete hydriding and dehydriding at 323 K; △, seven cycle after six previous complete hydriding and dehydriding cycles; ×, after 21 previous hydriding and dehydriding cycle ○, after annealing in vacuum at 693 K for 12h; ,after 22 previous hydriding and dehydriding cycles.

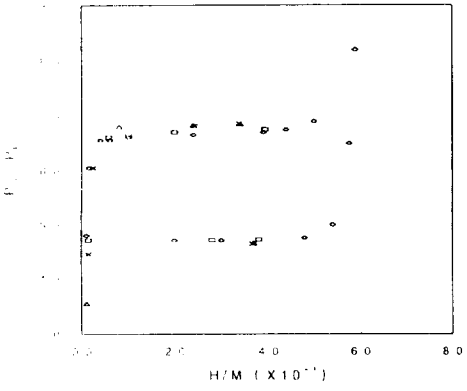

Fig. 3. Complete isotherms for Pd-H at 323 K. ◇, first cycle after annealing; □, second cycle after complete hydriding and dehydriding at 323 K; △, after nine previous complete hydriding and dehydriding cycles; ×, after 21 previous hydriding and dehydriding cycles.

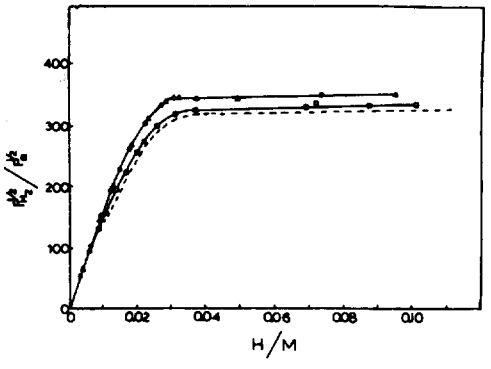

Fig. 4. Dilute phase hydrogen solubilities for several alloy forms at 323 K. ○, spin-cast form; △, rapidly quenched form; □, slowly quenched form; ----, annealed form.

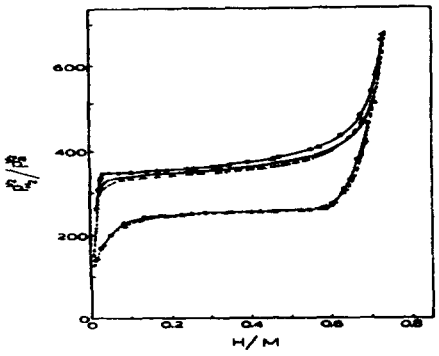

Fig. 5. Complete isotherms for several alloy forms at 323 K. ○, spin-cast form; △, rapidly quenched form; —, slowly quenched form; -----, annealed form. Open symbols for absorption and filled ones for desorption.

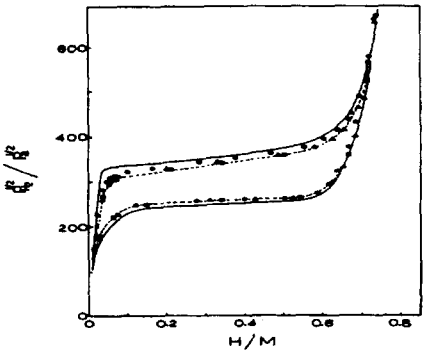

Fig. 6. Complete isotherms for the spin-cast alloy form showing the effect of repeated cycling without an intermediate annealing treatment. —, initial cycle; ○, second cycle; △, third cycle; □, fourth cycle; -----, seventh cycle. Open symbols for absorption and filled ones for desorption.

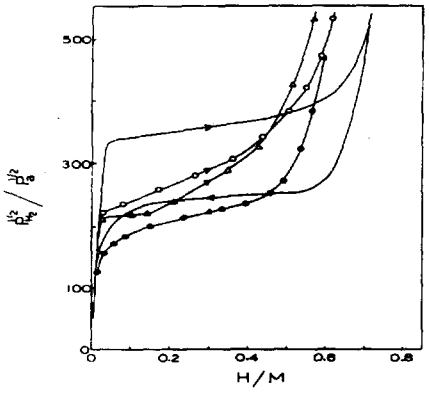

Fig. 7. Complete isotherms for the phase separated forms at 323K. —, rapidly cooled form; ○, heated form at 473 K for 1d in 123atm of H_2; △, heated form at 473 K for 5d in 123atm of H_2. Open symbols for absorption and filled ones for desorption.