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A Study of Hydrogen-Induced Metal Atom Rearrangement

Hak Noh, Choong-Nyeon Park[*], Ted B. Flanagan[**]

Automobile Research Center, Chonnam National University
300 Yongbong-Dong, Puk-Ku, Kwangju 500-757

[*]Dept. of Metallurgical Eng.,Chonnam National University
300 Yongbong-Dong, Puk-Ku, Kwangju 500-757

[**]Chemistry Department, University of Vermont, Burlington, VT 05405(USA)

abstract

Metal atom rearrangement has been shown to take place under the influence of hydrogen-induced atomic diffusion(HIAD) in initially homogeneous fcc palladiumalloys by electron microprobe analysis, optical microscopy, mechanical property tests and hydrogen isotherms. HIAD takes place in palladium alloys at moderate to elevated temperatures leading to phase segregation under conditions where segregation does not normally occur, i.e., in the absence of H over the time scale of the experiments. From these results, it is confirmed that dissolved hydrogen plays a dual role in some of these alloys, i.e. it catalyzes metal atom diffusion. This research demonstrates the potential utility of employing H-induced changes for phase diagram determination of Pd alloys and possibly for other alloy system.

1. Introduction

It is well known to those who carry out research on metal hydrogen systems that the reaction of $H_2(g)$ with solids can cause profound lattice changes. For example, in the amorphization of solids during hydrogenation, there is a change from a crystalline to an amorphous lattice, and in structural transition for Pd-Mn alloys[1], there is a change from disordered to ordered lattice. Such hydrogen-induced lattice rearrangements are of potential interest as a means for materials preparation. The primary purpose of the present research is to cite experimental evidence demonstrating the role of dissolved hydrogen in promoting lattice changes for Pd-based alloys.

The Pd-Rh system used in present research has a miscibility gap[2,3] but, as normally prepared by cooling from elevated temperatures starting above the miscibility gap, these alloys do not exhibit any evidence for segregation into Pd- and Rh-rich phases. Judging from their X-ray diffraction patterns, the alloys are random, homogeneous, fcc solid solutions over the whole composition range at ambient temperatures. After annealing it at 873K for one year, Raub[2] et. al.found that a $Pd_{0.74}Rh_{0.26}$ alloy did not segregate into Pd- and Rh-rich phases according to the X-ray diffraction pattern ; however, a $Pd_{0.49}Rh_{0.51}$ alloy did segregate into a two-phase mixture showing two sets of f.c.c. lattice parameters after annealing for 6 months at 873K.

Hydrogen absorption and desorption isotherms for Pd-Rh alloys have been determined by several workers[4,5,6,7], but in these studies the implications of phase segtregation were not considered. The f.c.c. lattice parameters of these Pd-Rh alloys decrease with increasing Rh content[5,8]. The enthalpies at infinite dilution, ΔH_H^0 were found to correspond to so-called contracted Pd alloy behavior, i.e. the ΔH_H^0 values are less exothermic than for Pd.

2. Experimental details

The Pd-Rh alloys were prepared by arc-melting the pure components under argon. The resulting alloy buttons were annealed at 1173K in vacuum for 72 hours and then rolled into thin foils of thickness of 140 μm which were re-annealed for 3days at 1173K for stress relief introduced by the rolling. The XRD patterns of these annealed alloys showed only one set of f.c.c. reflections.

Hydrogen absorption and desorption diagnostic isotherms were measured in a Sieverts, type apparatus with volumes which had been carefully calibrated ; the hydrogen-to-metal atom ratios were determined using the Beattie-Bridgman equation of state for hydrogen. The maximum H_2 pressure which could be employed in the hydrogen heat treatment(HHT) apparatus was about 55 atm at 873K. After HHT, samples were removed, cleaned and transferred to another for the diagnostic isotherm measurements.

Quantitative electron microprobe analysis of the specimens were made using electron microprobe analysis by a wavelength-dispersive spectrometer(WDS). Twenty points across the width of each foil were analyzed at approximately 5 μm intervals.

3. Results and Discussion

- Diagnostic Isotherms -

The complete diagnostic isotherms for relatively rapidly cooled and heat treated $Pd_{0.80}Rh_{0.20}$ alloys are shown in Fig. 1. A considerable difference can be seen in the diagnostic isotherms after hydrogen heat treatment at 873K for 4h ; both the capacity and plateau pressure have both markedly decreased. The hysteresis has vanished while it has not disappeared for an alloy heat treated in vacuum.

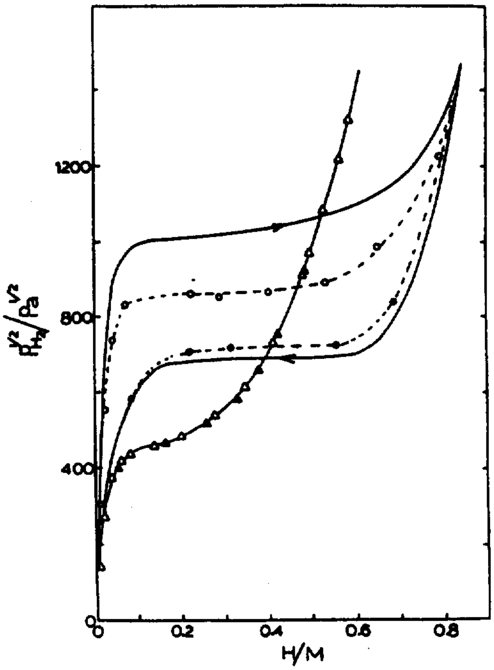

Fig. 1 P-C isotherms at 303K for the $Pd_{0.80}Rh_{0.20}$ alloy heated for 4h in vacuum and hydrogen : —,rapidly cooled ; ○, heated at 873K for 4h in vacuum; △, heated at 873K for 4h in 55 atm of hydrogen. Open symbols for absorption and filled ones for desorption.

After hydrogen heat treatment, the plateau pressure of the X_{Rh}=0.20 alloy was found to be closer to that of the X_{Rh}=0.13 alloy than to the original homogeneous X_{Rh}=0.20 alloy. The thermodynamic data for the H-treated $Pd_{0.80}Rh_{0.20}$ alloy also strongly support the view that the alloy has separated into a Pd-rich phase. It is concluded therefore that the metastable alloy almost completely segregated into Pd- and Rh-rich phases according to the estimated phase diagram.

- Compositional Analysis -

Compositional variations were analyzed before and after hydrogen heat treatment(HHT) and vacuum heat treatment(VHT) using electron microprobe analysis with an wavelength-dispersive spectrometer(WDS). Fig. 2 shows that both HHT and VHT introduce compositional variations but those found for HHT are much greater. Large and uniform composition changes

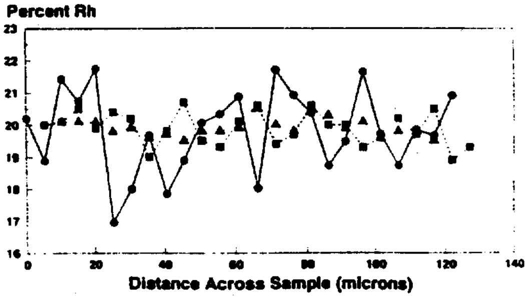

Fig. 2 Electron microprobe analysis of the $Pd_{0.80}Rh_{0.20}$ alloy. ▲, rapidly cooled ; ●, HHT for 4h at 873 K in 55 atm H2; ■, VHT for 4h at 873 K in vacuum.

such as might be expected from complete phase separation of the $Pd_{0.80}Rh_{0.20}$ alloy, $X_{Rh}=0.13$ and 0.87 at 873K, were not found because a relatively large area is sampled in the electron microprobe analytical method compared to the spacial extent of the phase separation.

-Physical Changes-

Physical changes were found after HHT such as increased hardness. The hardness and residual stress were measured for the $X_{Rh}=0.20$ alloy before and after HHT. The results for this alloy are shown in Table 1 where it can be seen that the hardness and residual stress both increase with the phase segregation resulting from HHT as reflected by changes in the diagnostic isotherms. A relatively linear relation obtains between 1/2 RT $\ln(P_f \times Pd)^{1/2}$ and the hardness ; $(P_f \times Pd)^{1/2}=P_{av}$ is an average plateau pressure and 1/2 RT $\ln P_{av}$ is then an average standard free energy change for hydride formation. Although the residual stress increases with decrease of 1/2 RT $\ln P_{av}$, the relation is not linear. The hardening and increased stress may result from regions of compositional inhomogeneity and accompanying dislocations introduced by the HHT despite the similar lattice parameters of Pd and Rh.

Table 1. Some Physical Property Changes Resulting from HHT for the $Pd_{0.80}Rh_{0.20}$ Alloy

HHT	Hardness/HK	-Residual Stress/MPa
none	143	0
873 K,4 h, 55 atm	350.1	409.5

4. Conclusions

In the present research the hydrogen-induced lattice changes occur throught the alloys resulting in some phase separation within the initially metastable, homogeneous Pd-Rh alloys. It is suggested that the phenomenon of hydrogen-induced lattice rearrangement in the present, somewhat nevel context, may prove to be generally useful for phase diagram determination, etc. The mechanism of these observations of H-induced lattice rearrangements may be related to the recent observation of Fukai and Okuma 10 that large concentrations of dissolved hydrogen, which can be obtained from ultra high hydrogen pressures at 873K, cause large vacancy concentrations to form in Pd or Ni. There are important results of this research which may be summarized as follows :

(a) only small amounts of dissolved hydrogen are needed to induce lattice changes at elevated temperatures; the small amounts needed would not be expected to significantly affect the binary equilibrium and therefore the lattice rearrangement corresponds to phase separation according to the phase diagram,

(b) the hardness and residual stress both increase with the phase separation,

(c) compositional variations are found using electron microprobe analysis and it is greater after HHT than after VHT,

(d) for the $X_{Rh}=0.20$ alloy at 873K, the Pd-rich phase boundary composition can be estimated after HHT from the plateau pressure ; the estimated composition agrees with the phase diagram.

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