

The Effect of the Ceramic Precipitates on the Hydrogen Solubility in Pd Alloys

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Abstract

Hydrogen solubility in internally oxidized Pd-Mo(Al) alloys has been studied at 323 K from the measurements of pressure-composition(p-c) isotherms. Internal oxidation of Pd_{0.985}Al_{0.015} and Pd_{0.97}Mo_{0.03} alloys results in the precipitation of Al and Mo particles in a matrix of pure Pd. It has been observed that the presence of the aluminum and molybdenum oxide precipitates results in an enhanced hydrogen solubility in the dilute phase region of Pd-H in a Pd/aluminum(molybdenum)oxide composites. Hydrogen solubility enhancements due to the presence of residual stresses around ceramic particles have been observed from p-c isotherms determined at 323 K after oxidation at 1073 K. The solubility enhancements in completely internally oxidized alloys are greater than that in partially oxidized alloys. The stress fields near the ceramic precipitates are the major source of the solubility enhancements. Transmission electron microscopy indicates that alumina precipitates are nanometer-sized and coherent with the Pd matrix after oxidation.

1. Introduction

If a homogeneous Pd alloy is exposed to an oxidizing environment at high temperature, preferential oxidation of the base-metal element contained in the alloy may occur inside the alloy if the solubility of oxygen in Pd is appreciable and the solute is present in small quantities. This is called internal oxidation and has been studied in a variety of noble metal-base metal alloy systems [1, 2]. In the case of Pd alloys, internal oxidation has been reported to occur in Pd-Zn[3], Pd-Zr[3], Pd-Mg[3], Pd-Cu[4], Pd-Al[3, 5, 6, 8] and Pd-Cr [7] systems. These substitutional fcc Pd alloys produce oxide precipitates within the metal phase on internal oxidation. In these studies, the interaction of dissolved hydrogen in palladium with these precipitates emphasize the use of hydrogen as a probe for characterizing the ceramic / metal interface. In these studies they devoted their attention to the low hydrogen content region where the hydrogen is trapped both irreversibly and reversibly at the interface. The irreversibly trapped hydrogen was believed to be bonded to unsaturated oxygen atoms at the interface forming an internal monolayer. This hydrogen could be removed by evacuation at the temperature higher than 573 K. The reversibly trapped hydrogen could be removed around 423 K and it was assumed to originate from a combination of segregation to the stress fields of the precipitates and interaction with chemical

species at the interface [3]. The limiting hydrogen content reached in their study was about $H/Pd=n=0.01$ where they noted that microcracks had formed at the corners of the large ceramic precipitates [8].

In the present study the effect of the ceramic precipitates on hydrogen solubility in the concentrated range, $H/Pd=n>0.01$, will be examined by gas phase measurements. The purpose is also to employ the hydrogen solubilities to learn about Pd containing internal ceramic precipitates. Hydrogen solubility in internally oxidized Pd alloys would be addressed in this communication. All the p-c isotherms of palladium and Pd-Mo(Al) alloys exhibited plateau pressure regions where a dilute and hydride phase co-exist[9].

2. Experimental

The Pd-Mo(Al) substitutional alloys were arc-melted under argon. The buttons were flipped and re-melted several times for homogeneity. They were then well-annealed in vacuum for 3 days at 1133 K, rolled into foils and then re-annealed for 2 days at 1133 K to remove stress produced from rolling. Pressure-composition(p-c) isotherms were determined for the Pd-Mo(Al) alloys at 323 K. Heat treatment for internal oxidation was carried out in air at various temperatures from 983 K to 1273 K for various lengths of time. After oxidation treatment, the alloys were cleaned with emery paper in order to remove a thin

oxide layer. P-C isotherm measurements for heat-treated Pd alloys were carried out in a Sievert's type apparatus at 323 K. In the dilute hydrogen solution region (α), the p-c isotherms were also measured after evacuating the chamber before the two phase region ($\alpha + \beta$) was reached to eliminate irreversible trapping behavior in the second run.

The microstructures of the internally oxidized Pd_{0.985}Al_{0.015} was determined by optical and transmission electron microscopy (TEM). It was not possible to resolve the alumina precipitates by optical microscopy. Thin foils for TEM were prepared from Pd_{0.985}Al_{0.015} after oxidation for 72h at 1073 K by jet polishing and TEM was carried out using a Hitachi H-800 electron microscope operating at 100 kV.

3. Results and Discussion

3.1. Transmission electron microscopy of internally oxidized alloy

The microstructure of the internally oxidized Pd_{0.985}Al_{0.015} alloy after oxidation for 72h at 1073 K is shown in Fig. 1. Alumina precipitates in Pd have a form of triangular prism, and they were founded from the measurement of the diagnostic p-c isotherm. The shape and size of the Al precipitates observed in the present study are similar to that reported by Eastman [6] who also reported that alumina precipitates coherently with matrix. Moreover, it appears that the alumina is present as fine nanocrystalline precipitates.

It can also be noticed in Fig. 1 that the Pd matrix surrounding the alumina precipitates are free of dislocations. Moreover, dislocations are also absent at the alumina-palladium interface after oxidation treatment and this had been noted by Eastman [6] earlier. The absence of dislocations generated near the ceramic-matrix interface has also been found by transmission electron microscopy in other composite systems [10, 11].

3.2. P-C Isotherms (Dilute Phase) for the Unoxidized Pd-Mo (Al)Alloys

The p-c isotherms in the dilute solid solution of hydrogen in the metal (dilute phase) for Pd_{0.985}Al_{0.015} and Pd_{0.97}Mo_{0.03} alloys and pure Pd are shown in Fig. 2. The results for the alloys generally agree with the study of Sakamoto et al [9] who find that the low pressure solubilities decrease and the terminal hydrogen solubilities increase with increasing substitutional elements. There is negligible difference between the dilute phase solubilities of Pd and Pd_{0.985}Al_{0.015} alloy because of the low solute content. However, the hydrogen solubilities in dilute region for Pd_{0.97}Mo_{0.03} alloy is higher than that of pure Pd. Also, the terminal hydrogen solubilities are greater for the both alloys. An enhancement in solubility of hydrogen should be occurred from internal oxidation in metal matrix.

3.3. P-C Isotherms for the oxidized Alloys

The p-c isotherms at 323 K for the

Pure Pd, unoxidized and oxidized $\text{Pd}_{0.985}\text{Al}_{0.015}$ alloy at 1073 K for 72h in air are shown in Fig. 3. For the foil thickness employed here complete internal oxidation takes place under these conditions. The higher pressure isotherm corresponds to the alloy before its oxidation. The isotherms measured before and after oxidation show that the hydrogen capacity increases and the plateau pressure decreases after oxidation. The plateau pressure after oxidation corresponds almost closely to that of pure Pd-H systems. After oxidation treatment, the hysteresis is essentially unchanged from pure Pd-H. It also should be noted that the plateaux are more horizontal for the fully oxidized alloy than normally observed for the Pd-H foils where the plateau pressures increase when the H content is about half way along the plateau. The difference may be due to the relief of some internal macroscopic strain in the former due to the microcracks.

Fig. 4 shows p-c isotherms for $\text{Pd}_{0.97}\text{Mo}_{0.03}$ alloy before and after oxidation treatment at 1073K for 72h in air. It was shown earlier that the extent internal oxidation of Pd-Al alloys can be conveniently determined using p-c isotherms measured at moderate temperatures after oxidation [12]. An examples of this is also shown in this figure by the diagnostic p-c isotherm obtained after internal oxidation. After oxidation at 1073K for 72h, there are two split plateau pressures in absorption curve and it is indicating incomplete oxidation. The initial, lowest plateau pressure

corresponds to pure Pd and the higher plateau pressure is for unoxidized some Pd-Mo alloys. The result proves that the volume fraction of oxidation can be estimated by diagnostic p-c isotherm. For example, the width of the Pd-H plateau in this figure divided by the width of the plateau for pure Pd provides the fraction of Pd-Mo alloy that has been converted to the oxide. The depth of the penetration of the front can be easily measured from the known thickness of the specimen (~ 125 μm). Knowing the depth of penetration as a function of oxidation time at a fixed temperature, the permeability of oxygen in Pd was determined [12].

4. Conclusion

The internal oxidation of Pd-Al(Mo) alloys results in alumina and molybdenum oxide precipitates in the Pd matrix. It has been observed that the presence of the alumina and molybdenum oxide precipitates results in an enhanced hydrogen solubility in the dilute phase region of Pd-H for a Pd/Al(Mo) oxide composites. Hydrogen solubility enhancements due to the presence of residual stresses around ceramic particles have been observed from diagnostic p-c isotherms determined at 323 K after oxidation at 1073 K. The solubility enhancements in completely internally oxidized alloys are greater than that in partially oxidized alloys. The stress fields around the ceramic precipitates are the major source of the solubility enhancement.

The microstructure of the internally oxidized Pd_{0.985}Al_{0.015} alloy after oxidation for 72h at 1073 K shows that alumina precipitates in Pd has a form of triangular prism. Moreover, it appears that the alumina is present as fine nanocrystalline precipitates and coherent with the Pd matrix after oxidation.

Acknowledgements

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Fig. 1. Transmission electron micrograph showing faceted alumina precipitates formed in Pd during internal oxidation for Pd_{0.985}Al_{0.015} alloy

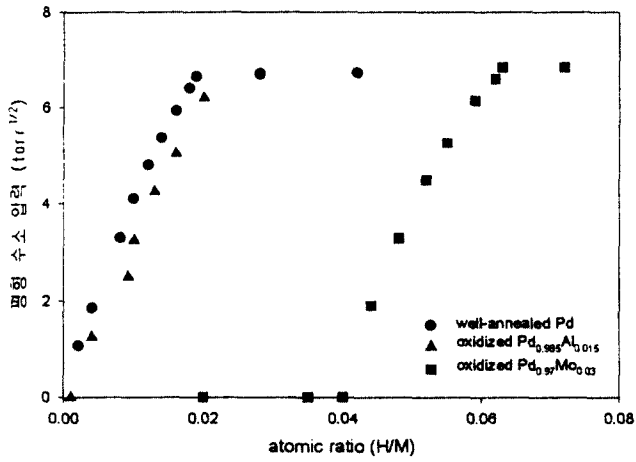


Fig. 2. P-C isotherms in dilute phase at 50°C for oxidized Pd alloys

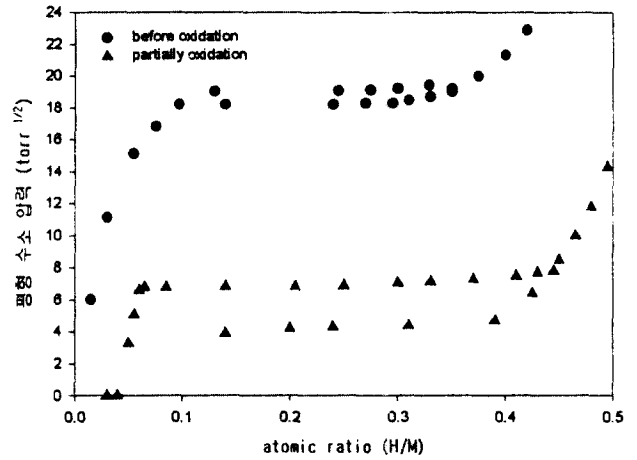


Fig. 4. P-C isotherms at 50°C for Pd_{0.97}Mo_{0.03} alloy.

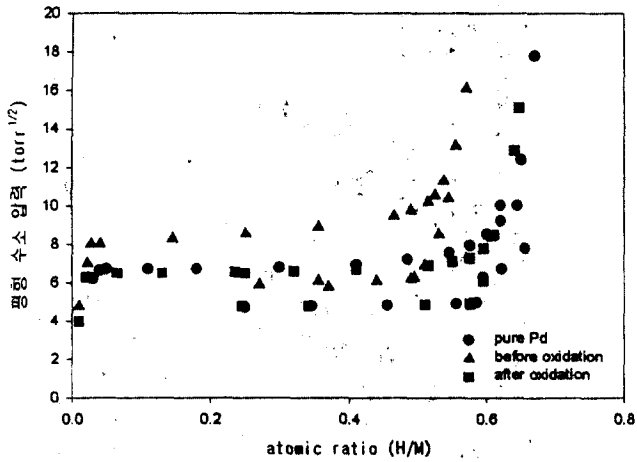


Fig. 3. P-C isotherms at 50°C for Pd_{0.985}Al_{0.015} alloys