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Some microstructural aspects of hydriding internally oxidized Pd–Al alloys

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Abstract

Microstructural studies of internally oxidized Pd–Al alloys have been carried out using scanning electron microscopy. Pd nodules form by extrusion of Pd from the bulk while vacancies are transported from the surface during the formation of the internal oxide precipitates. The result is a dimpled honeycomb appearance in the subsurface region as seen along grain walls. Extensive intergranular cracking occurs during internal oxidation. When the internally oxidized alloys are hydrided/dehydrided, cracking is accentuated with transgranular cracks developing. Significant enhancement in the rates of hydriding and dehydriding have been observed after internal oxidation. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Internal oxidation; Microstructure; Scanning electron microscopy; Hydriding and dehydriding rate

1. Introduction

Internal oxidation (IO) occurs in an alloy composed of a solute which is more readily oxidizable than the solvent metal. At elevated temperature oxygen dissolves into such an alloy leading to internal oxidation where the solute oxide precipitates internally [1]. IO proceeds by inward movement of the internal oxidation zone. IO behavior of a wide variety of alloys based on Cu, Ag and Pd has been reported in the literature [1].

The IO of Pd–Al alloys and their subsequent interaction with H_2 have been studied by Huang et al. [2], Noh et al. [3] and Balasubramaniam et al. [4]. It was shown that the extent of internal oxidation of these Pd–Al alloys could be conveniently followed by the use of $p_{H_2}(g)$ – H content isotherms [3]. Moreover, the nature of the interface between the metal and the internal oxide and the surrounding stress field can be probed using dissolved H in equilibrium with $p_{H_2}(g)$ [2,4].

Transmission electron photomicrographs (TEM) of internally oxidized Pd–Al alloys have been shown elsewhere [3,5,6]. The sizes of the alumina precipitates were greater after IO at 1273 K than at 1073 K [4]. The approximate sizes of the precipitates can be estimated at the various oxidation temperatures as: 100 nm (1273 K), 30 nm (1073 K) and <10 nm (983 K). Those formed by oxidation at 983 K were too small to be characterized by conventional TEM and their size was estimated from the amount of irreversibly trapped H [6]. After oxidation at the above temperatures, TEM did not reveal any dislocations associated with the precipitates [4,5].

It was recently observed that the kinetics of H_2 absorption by Pd–Al alloys are enhanced after internal oxidation [4]. In view of the importance of the kinetics of H_2 absorption in applications of M–H systems, and the key role of the surface and sub-surface layers in the kinetics, a detailed examination of the microstructures of the internally oxidized Pd–Al alloys has been undertaken. Some aspects of the investigation are presented in this paper.

2. Experimental procedure

Pd–Al alloys of compositions $X_{Al}<0.05$ were prepared by arc-melting the pure elements, annealing the buttons, and then rolling into foil of about 2 cm×0.3 cm×110 μm. They were then oxidized in the atmosphere in a tube furnace after which they could be either slowly cooled or quenched from the oxidation temperature. The latter was generally employed because the time of oxidation could then be more accurately controlled. The oxidation percentage was determined from the weight gain and/or H_2 absorption isotherms [3]. The latter is more accurate and the former, although more convenient, generally yields somewhat too high values at the lower temperatures of oxidation where Pd itself oxidizes, i.e., at ≤ 1150 K. For

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determining the rate curve, 1.7 g of the material was used in a reaction vessel of volume 71 cc and the change in pressure was monitored after admitting high purity hydrogen.

The cross-sections of the oxidized alloys before and after hydriding were examined by scanning electron microscopy (SEM). The compositions of select features were obtained by energy dispersive analysis by x-rays (EDAX) unit attached to the SEM. The samples were mounted in cold-setting epoxy, ground and polished to a 0.3 μm finish and then etched (1 h) in a solution of KI and KCN and ultrasonically cleaned in distilled water. The surfaces of the foils were also observed by SEM.

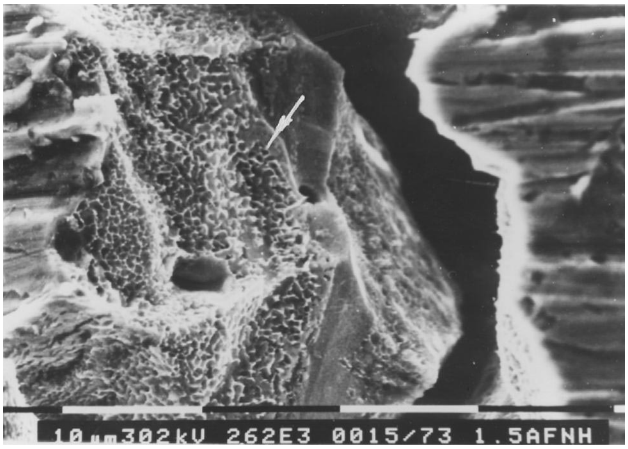

Fig. 2. A 100% oxidized $Pd_{0.985}Al_{0.015}$ alloy is found to have intergranular cracking throughout the sample. The grain walls generally exhibit a dimpled appearing structure (arrowed).

3. Results and discussion

3.1. SEM of internally oxidized Pd/Al alloys

Fig. 1 shows a cross-sectional micrograph of a $Pd_{0.97}Al_{0.03}$ alloy which has been partially oxidized (50%) but not hydrided. The internally oxidized portion has a different texture from the unoxidized portion as a result of their different degree of etching. Within the oxidized region intergranular cracking is seen especially at the edges and corners of the samples. The internally oxidized zone front is seen to be curved intersecting the intergranular cracks which end at the boundary. The extent of IO can be calculated approximately from the penetration shown by SEM (Fig. 1) and this agrees with that determined from the p_{H_2} isotherms [3]. A 100% oxidized $Pd_{0.985}Al_{0.015}$ alloy is found from SEM to have intergranular cracking throughout the sample. The SEM of the grain walls of this alloy is shown to have a dimpled appearing structure (Fig. 2). The dimpled appearing grain boundaries should exist up to the internal oxidation front. This is a new observation of such an internally oxidized alloy and has implications for the enhanced kinetics of H_2 absorption by internally oxidized Pd–Al alloys.

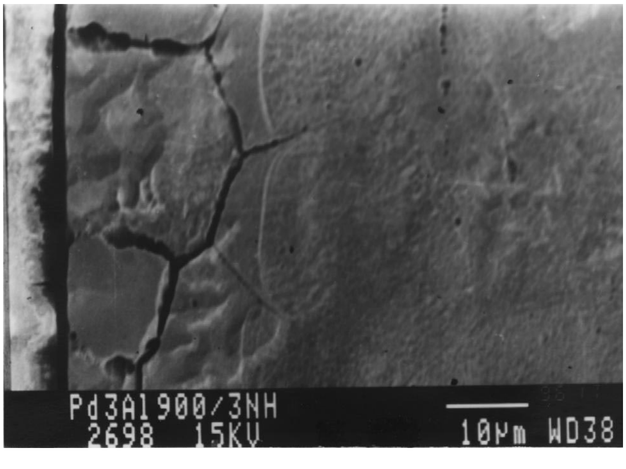

Fig. 1. Cross-sectional micrograph of a $Pd_{0.97}Al_{0.03}$ alloy which has been partially oxidized (50%) but not hydrided.

In order to understand the nature of the cracking and the structure, the surfaces of the specimens were observed by SEM. A general characteristic noticed in the specimens was that they were rough due to surface scratches. The oxide of Pd (PdO) covered the surface when the temperature of oxidation was below the decomposition temperature of PdO. In locations where the PdO had been peeled off, underlying Pd nodules could be observed.

Faceted alumina precipitates, that appear white in color in Fig. 3, could be identified individually on the thermally grooved surface of an internally oxidized (100%) $Pd_{0.985}Al_{0.015}$ at 1073 K. Their composition was confirmed by EDAX. The surface also had small nodular structures which were identified as PdO. These nodular PdO oxides could be seen only at much higher magnifications and cannot be seen in Fig. 3. The dissociation pressure of PdO reaches 1 atm. at 1150 K [7] and therefore oxidation of Pd

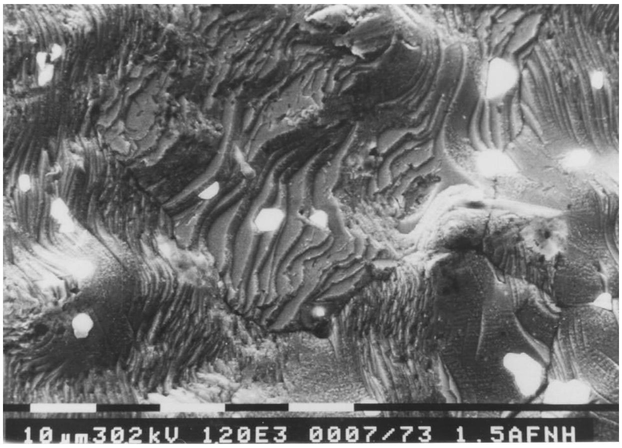

Fig. 3. Surface of an internally oxidized $Pd_{0.985}Al_{0.015}$ at 1073 K (100%) showing faceted alumina precipitates (appearing white) and thermal grooves.

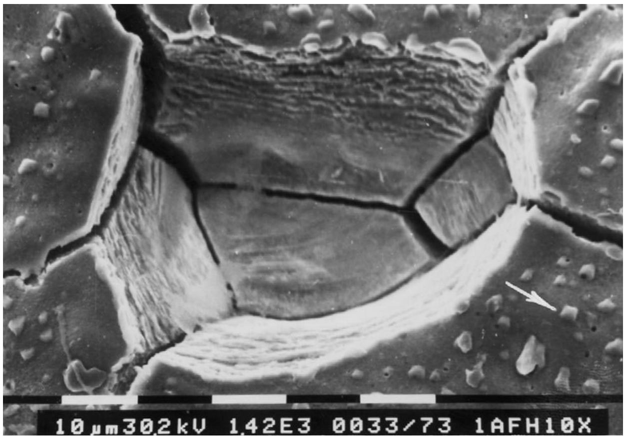

Fig. 4. Surface structure of a $Pd_{0.985}Al_{0.015}$ alloy that has been completely internally oxidized at 1073 K and cycled ten times. The faceted nodules (one such nodule is arrowed) were compositionally analyzed to be pure Pd. Note the presence of pores below the nodules and the nodule-free-zone next to the grain boundaries.

to PdO is thermodynamically possible under the IO conditions, i.e., 1073 K.

3.2. SEM of internally oxidized Pd/Al alloys which had been subsequently cycled

A 40% oxidized $Pd_{0.97}Al_{0.03}$ alloy shows more pronounced cracking in its oxidized fraction after cycling than before and some grains appear to be missing or partially removed from the plane of the specimen. It was also observed from surface SEM studies that on repeated cycling, some cracking occurs transgranularly. For comparison, SEM was carried out on cycled (323 K) pure Pd; this showed no extensive cracking and therefore it is clear that the cracking arises from cycling in the presence of the immobile oxide precipitates.

The surface of a 100% internally oxidized $Pd_{0.985}Al_{0.015}$ alloy after cycling ten times is shown in Fig. 4 where a grain is missing revealing dimpled walls and underlying internal cracking. Faceted nodules with characteristic shapes, as seen on the surface, were analyzed using EDAX as pure Pd. It can be clearly seen in other SEM photographs that directly under Pd nodules, long pores may be noticed. This was found almost universally. These long pores are the pathways along which Pd atoms diffuse out on to the surface to form nodules.

Mackert et al. [8] first observed Pd–Ag nodules on the surface after IO of a Pd–Ag based dental alloy containing small amounts of oxidizable Sn and In. They noted that the volume of the surface nodules were closely equal to the total volume increase associated with the internal oxides [8]. In the present case, Pd nodules are also observed when Pd–Al alloys are internally oxidized.

3.3. Cracking and kinetics of hydride formation

Intergranular cracking developed during the process of IO (Fig. 1) and this was accentuated during hydrogen cycling with the appearance of some transgranular cracking. A typical comparison of the p_{H_2} versus t plots at 273 K for mechanically cleaned Pd foil to an internally oxidized $Pd_{0.97}Al_{0.03}$ at 1073 K (100%) is shown in Fig. 5. The

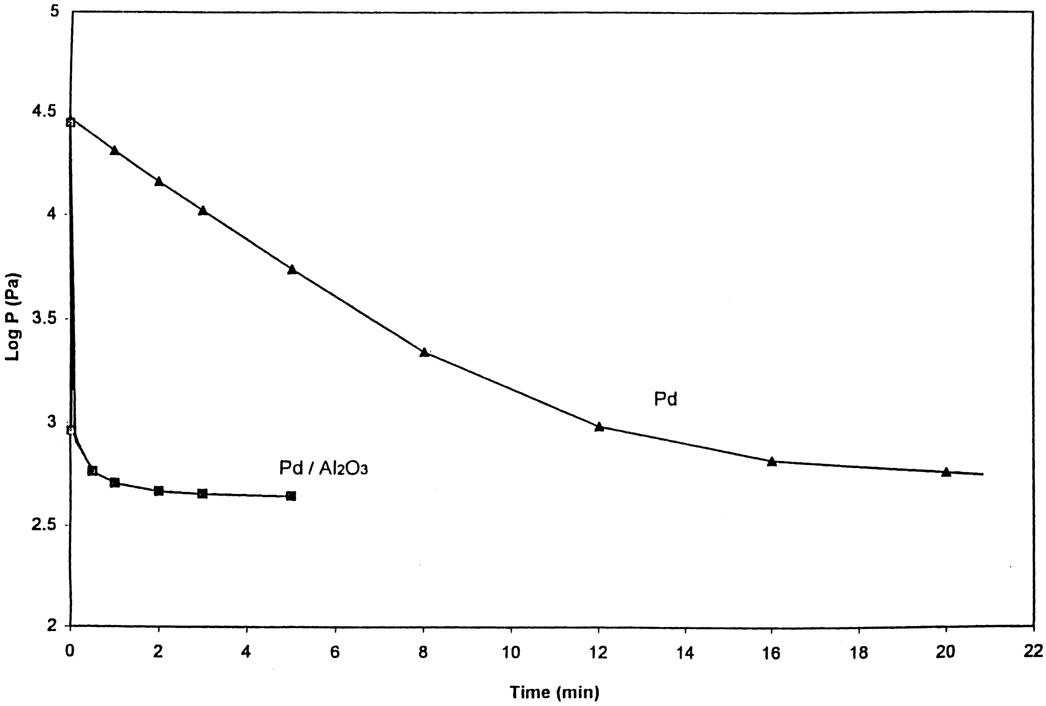

Fig. 5. A typical comparison of the p_{H_2} versus t plots at 273 K for mechanically cleaned Pd foil to $Pd_{0.97}Al_{0.03}$ internally oxidized 100% at 1073 K.

dramatic difference in rates for reaching the equilibrium hydrogen pressure must be related to the cracking and enhanced surface area which are developed as a result of IO. It is also conceivable that the Pd/Al_2O_3 interaction plays a role as it does in Pd/Al_2O_3 heterogeneous catalysts where Pd is the minority species [9].

4. Conclusions

The microstructure of internally oxidized Pd–Al alloys has been observed before and after hydriding. Pd nodules are observed to have been extruded onto the surface resulting from the formation of internal oxide precipitates. Accompanying the formation of these nodules is the formation of a dimpled, honeycombed grain boundary and porous subsurface structure (Fig. 4). The virgin alloys crack intergranularly after IO and the extent of cracking after IO can be used to monitor its extent in these thin samples. After hydriding the internally oxidized alloys, some transgranular cracking is observed. The formation of the porous subsurface layer after IO may be related to the significant enhancement observed in the rates of hydriding and dehydriding.

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