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Hydrogen diffusivity and solubility in palladium alloys

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Abstract

Samples of $Pd_{0.97}Al_{0.03}$, $Pd_{0.9}Pt_{0.1}$ and $(Pd_{0.9}Pt_{0.1})_{0.97}Al_{0.03}$ alloys, cold worked and internally oxidized at 1073 K for 72 h were submitted to a hydrogen permeation test at 313 K, using two levels of cathodic charging current for hydrogen generation, equal to 0.1 and 20 mA. The effects of internal oxidation were investigated by X-ray diffraction and transmission electron microscopy (TEM). The formation of prismatic nano-precipitates of Al_2O_3 was observed by TEM analyses in $Pd_{0.97}Al_{0.03}$. However, in the $(Pd_{0.9}Pt_{0.1})_{0.97}Al_{0.03}$ alloy, the formation of Al_2O_3 was not observed, which suggests that the addition of Pt to Pd–Al inhibits the internal oxidization of Al. Cold work and addition of Al and Pt to Pd contribute to decrease the hydrogen diffusion coefficient, but, on the other hand, increase the apparent hydrogen solubility, S_{app}. This increase is more effective for $Pd_{0.97}Al_{0.03}$ sample where $S_{app}=1075$ mol H m^{-3}. A great deviation in the hydrogen permeation curve, performed at 20 mA, was observed for $Pd_{0.97}Al_{0.03}$ internally oxidized, which indicated hydride formation during the test. This behavior was observed for oxidized $Pd_{0.97}Al_{0.03}$ but not for the $(Pd_{0.9}Pt_{0.1})_{0.97}Al_{0.03}$ alloy.

Keywords: Hydrogen diffusion; Hydride; Internal oxidation

1. Introduction

The hydrogen–palladium alloy systems have been well studied due to their excellent interaction and properties. Nowadays, great attention has been paid to binary and ternary palladium alloys. Pd-based alloys containing small amounts of oxidizable solute metals such as Al, Mg, Zn and Zr have been characterized using hydrogen as a probe [1–4]. In the Pd matrix, the products of oxidization generally result in nano-sized oxide precipitates.

Huang et al. [1], using a hydrogen diffusion technique in different Pd-rich alloys, have analyzed the interaction between hydrogen and the traps in the internally oxidized microstructure. The simple presence of the metallic elements dissolved in the Pd matrix as well as the oxidation of these elements contributes to elevate the amount of hydrogen trapped in the alloy. Balasubramaniam et al. [2] proposed the use of a hydrogen isotherm as a convenient method for monitoring the progress of internal oxidation of Pd-rich binary alloys. They observed that for the Pd alloys containing small additions of solute metals, the isotherms can be used to characterize the alloy and its degree of homogeneity.

The interaction between hydrogen and the microstructure can also be studied by hydrogen permeation tests [5–7]. Hydrogen diffusivity and solubility of the alloys are affected due to the existence of dispersed phases like fine precipitates or structural defects such as vacancies and dislocations.

In this work, we present hydrogen permeation results obtained by applying low and high cathodic charging currents to $Pd_{0.9}Pt_{0.1}$, $Pd_{0.97}Al_{0.03}$ and $(Pd_{0.9}Pt_{0.1})_{0.97}Al_{0.03}$ cold worked and heat treated at 1073 K for 72 h to promote internal oxidation.

2. Experimental techniques

Buttons of the $Pd_{0.97}Al_{0.03}$, $Pd_{0.9}Pt_{0.1}$ and $(Pd_{0.9}Pt_{0.1})_{0.97}Al_{0.03}$ alloys were prepared by arc-melting from the pure elements. The products of the melt were cold worked in the form of foils. The alloys containing Al were heat treated for 72 h at 1073 K in air to promote internal oxidation of this element. Pure Pd, cold worked and annealed for 1 h at 1073 K, were also submitted to

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hydrogen permeation tests for comparison with the alloys produced in this work.

After the heat treatment of internal oxidation, samples of $Pd_{0.97}Al_{0.03}$ and $(Pd_{0.9}Pt_{0.1})_{0.97}Al_{0.03}$, in disks of 3 mm diameter were prepared by using ion milling for transmission electron microscopy (TEM) analysis which was performed using a Philips 300 kV microscope.

Samples of 10×10 mm dimension were submitted to electrochemical hydrogen permeation tests at 313 K, using a solution of 0.1 M NaOH as electrolyte as described elsewhere [5]. These tests were undertaken using an electrochemical cell comprising two compartments separated by the sample. In one of them, a constant cathodic current was applied to generate hydrogen at the surface of the metal foil. In the other compartment, a weak anodic potential was applied to oxidize the hydrogen that permeates through the sample. For each sample, the following values of cathodic current were applied for hydrogen generation: 0.1 mA (2.15 A m^{-2}) and 20.0 mA (430 A m^{-2}).

The evolution of hydrogen flux $J_L(t)$ with time (t), exhibits a sigmoidal relationship. Assuming the diffusivity of hydrogen not to vary with the hydrogen concentration, this current may be expressed as [6]:

$$J_L(t) = J_\infty \left\{ 1 - \frac{4}{\pi} \sum_{0}^{\omega} \frac{(-1)}{2n+1} \exp\left[\frac{-(2n+1)^2 \pi^2 D_{app} t}{4L^2} \right] \right\} \tag{1}$$

where J_∞ is the steady state current, D_{app} is the apparent hydrogen diffusivity, L is the sample thickness.

The apparent hydrogen solubility is determined by applying the follow equation:

$$S_{app} = \frac{J_\infty L}{D_{app}} \tag{2}$$

3. Results and discussion

Fig. 1 shows the TEM figure for $Pd_{0.97}Al_{0.03}$ internally oxidized for 72 h at 1073 K where one can be observe the formation of prismatic nano-precipitates of Al_2O_3 of about 20 nm in size. For $(Pd_{0.9}Pt_{0.1})_{0.97}Al_{0.03}$ the presence of Al_2O_3 in the Pd matrix was not observed.

Fig. 2 shows hydrogen permeation curves at 313 K obtained for $Pd_{0.9}Pt_{0.1}$, $Pd_{0.97}Al_{0.03}$ and $(Pd_{0.9}Pt_{0.1})_{0.97}Al_{0.03}$ and also pure Pd under annealed and cold worked conditions. The curves were normalized by the value of maximum flux of each curve. It can be observed in Fig. 2 that the addition of Pt and Al induces an increase in time of the hydrogen permeation, which represents a lowering of hydrogen diffusivity. This reduction is more pronounced for the $Pd_{0.97}Al_{0.03}$ alloy in comparison to $Pd_{0.9}Pt_{0.1}$, although the addition of Pt in the Pd is greatest. This behavior can be explained as a function of atomic radius of each element, which promotes an important distortion in the neighborhood that promotes trapping for hydrogen [8]. As Pt possesses a atomic radius close to Pd, the distortion due to physical nature is smaller than in the case of Al where the atomic radius is greater than that of Pt. This effect was observed for another Pd alloys [9]. Other effects such as valence and local stressing must also be considered.

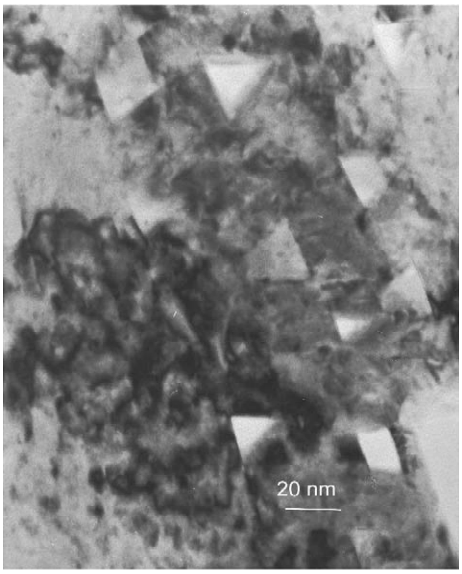

Fig. 1. TEM micrograph of internally oxidized $Pd_{0.97}Al_{0.03}$ for 72 h at 1073 K, showing the Al_2O_3 formation.

It is also observed in Fig. 2 that the cold work decreases hydrogen diffusion coefficient. This is due to multiplication of dislocations and generation of vacancies during cold work which trap the hydrogen in the reversible and irreversible way depending of nature of defect [10]. Table

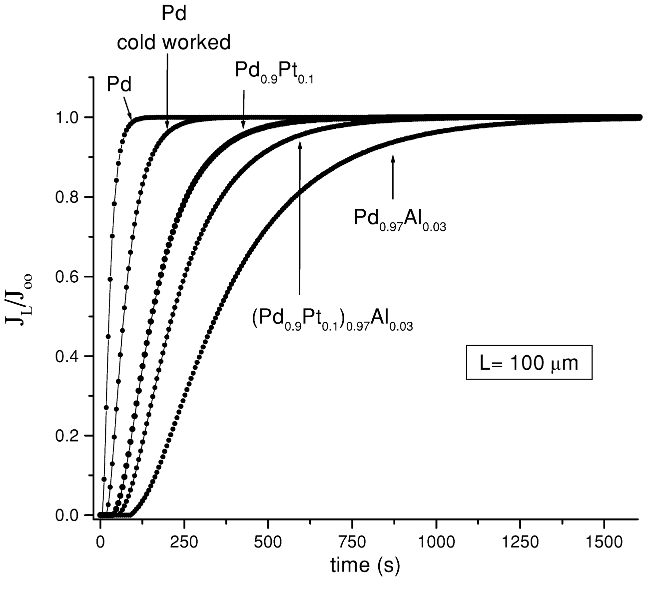

Fig. 2. Hydrogen permeation curves for pure Pd and Pd alloys obtained at 313 K with hydrogen cathodic charging of 0.1 mA.

Table 1
Hydrogen parameters permeation of pure Pd and Pd alloys at 313 K for cathodic charging equal to 0.1 mA

Alloy	L (μm)	D_{app} ($m^2\ s^{-1}$)	S_{app} (mol H m^{-3})
Pd (annealed)	200	5.5×10^{-11}	60
Pd (cold worked)	200	2.0×10^{-11}	135
$Pd_{0.9}Pt_{0.1}$ (melted and cold work)	150	0.9×10^{-11}	230
$Pd_{0.97}Al_{0.03}$ (melted and cold work)	120	0.4×10^{-11}	695
$Pd_{0.97}Al_{0.03}$ (oxidized for 72 h at 800 °C)	120	0.2×10^{-11}	1075
$(Pd_{0.9}Pt_{0.1})_{0.97}Al_{0.03}$ (melted and cold work)	70	0.7×10^{-11}	360
$(Pd_{0.9}Pt_{0.1})_{0.97}Al_{0.03}$ (oxidized for 72 h at 800 °C)	70	1.4×10^{-11}	170

1 presents apparent hydrogen diffusivity and solubility values for these alloys. One can notice a decrease of more then 50% in D_{app} for pure Pd cold worked $D_{app}=5\times10^{-11}$ $m^2\ s^{-1}$ (annealed) and $D_{app}=2\times10^{-11}$ $m^2\ s^{-1}$ (cold worked). However, these reductions are more significant when solute atoms Pt and Al are present.

Small additions of substitutional dissolved metals often have only slight effects on the hydrogen diffusivity in the palladium [8]. This is due to the repulsive interaction force between hydrogen atoms and substitutional impurity atoms. This happens because the interaction of hydrogen with impurities is less pronounced compared to Pd atoms and the interstitial sites around these impurities, which may be described as anti-trapping sites [8]. In general, traps play an important role in metals and alloys where the mobility of hydrogen is drastically reduced by the effects of interaction with traps and hydrogen. For palladium in general, a slight enhancement of the solubility and a small decrease of hydrogen diffusivity for cold worked samples has been observed [10].

Fig. 3 shows the hydrogen permeation curves for $Pd_{0.97}Al_{0.03}$ and $(Pd_{0.9}Pt_{0.1})_{0.97}Al_{0.03}$ cold worked and oxidized for 72 h at 1073 K. It is observed in Fig. 3 that the two alloys have different effects. For the $Pd_{0.97}Al_{0.03}$ alloy, internal oxidation promotes lowering of about 50% in the D_{app} (from 0.4 to 0.2×10^{-11} $m^2\ s^{-1}$). However, for the internally oxidized $(Pd_{0.9}Pt_{0.1})_{0.97}Al_{0.03}$ alloy an increase in D_{app} in the alloy (from 0.7 to 1.4×10^{-11} $m^2\ s^{-1}$) was observed. This is attributed to the ability of Pt to inhibit the formation of Al_2O_3 precipitate and also because the heat treatment for a long time at high temperature to promote the oxidation of the $(Pd_{0.9}Pt_{0.1})_{0.97}Al_{0.03}$ is capable of provoking an annihilation of the trap sites of the hydrogen and consequently an increase in the hydrogen diffusivity.

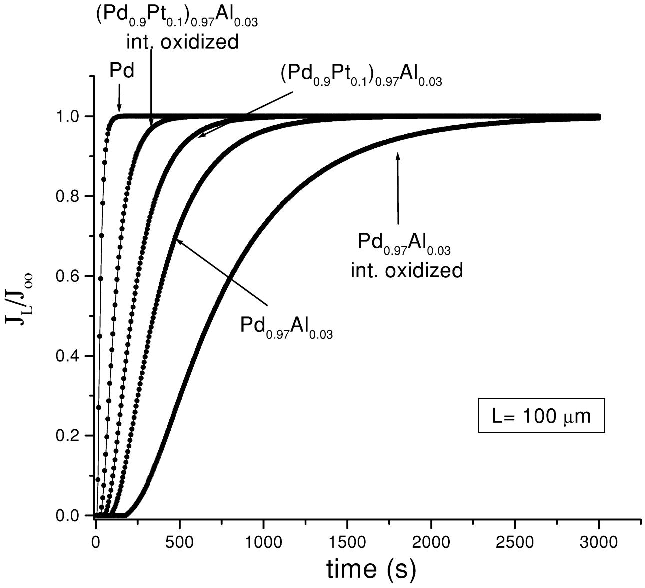

Fig. 3. Hydrogen permeation curves, obtained at 313 K for pure Pd and Pd alloys internally oxidized for 72 h at 1073 K, with hydrogen cathodic charging of 0.1 mA.

Concerning the hydrogen solubility in the Pd and Pd alloys analyzed, it can be observed that cold work increases the quantity of hydrogen stored (Table 1). This increase is more pronounced in the alloys containing solid solution because of interaction between solute atoms and dislocations during the cold work, increasing the concentration of defects in the metals.

It is observed that solubility of hydrogen in pure Pd when cold worked ($S_{app}=135$ mol H m^{-3}) is higher than Pd annealed ($S_{app}=60$ mol H m^{-3}). For $Pd_{0.97}Al_{0.03}$ alloy melted and then cold worked, solubility increases markedly ($S_{app}=695$ mol H m^{-3}), especially due to the effect of lattice distortion and interaction of solute atoms and screw dislocation [8]. However, when the Pd–Al alloy is oxidized and coherent precipitates are formed, additional sites of irreversible nature which trap the hydrogen are created and then, the solubility increases more expressively ($S_{app}=$ 1075 mol H m^{-3}). In the case of the $(Pd_{0.9}Pt_{0.1})_{0.97}Al_{0.03}$ alloy, the effect of two solute atoms in the Pd matrix are competing and the solubility increases, but not markedly ($S_{app}=360$ mol H m^{-3}). This can be attributed to the similarity between atomic radius of Pd and Pt. However, in the internally oxidized $(Pd_{0.9}Pt_{0.1})_{0.97}Al_{0.03}$ alloy, Al_2O_3 is not observed by TEM analysis. In this case, the trap sites of hydrogen are annihilated, causing a decrease in the apparent hydrogen solubility ($S_{app}=170$ mol H m^{-3}).

3.1. Hydride formation

It is very well know that Pd and Pd alloys, when submitted to a high hydrogen charging, can form hydride. The characterization of hydride in metals can be easily performed by X-ray diffraction. In the electrochemical hydrogen permeation tests, hydride can be identified by means of curves that reveal a double sigmoid shape [5,7].

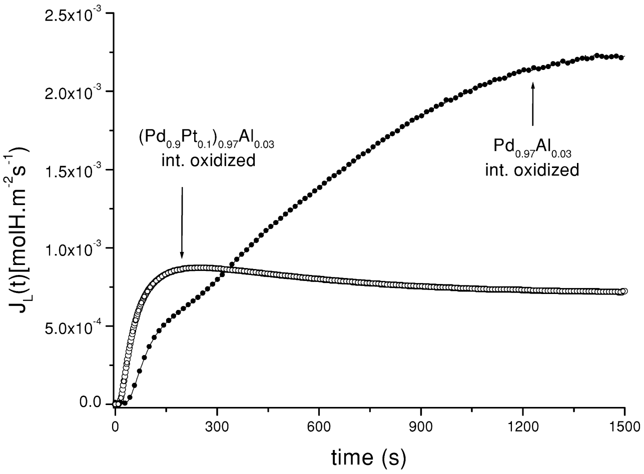

Fig. 4. Hydrogen permeation curves obtained at 313 K, for $Pd_{0.97}Al_{0.03}$ and $(Pd_{0.9}Pt_{0.1})_{0.97}Al_{0.03}$ internally oxidized for 72 h at 1073 K.

Fig. 4 shows the hydrogen permeation curves, obtained at 313 K with a high cathodic charging equal to 20 mA for internally oxidized $Pd_{0.97}Al_{0.03}$ and $(Pd_{0.9}Pt_{0.1})_{0.97}Al_{0.03}$. It can be observed in Fig. 4 that the hydrogen permeation curve for $Pd_{0.97}Al_{0.03}$ possesses a double-sigmoidal shape, while, for the $(Pd_{0.9}Pt_{0.1})_{0.97}Al_{0.03}$ alloy, the hydrogen permeation curve possesses a very well defined sigmoidal shape. This suggests that the Pt addition increases the resistance to hydride formation in the $(Pd_{0.9}Pt_{0.1})_{0.97}Al_{0.03}$ alloy. This result is in accordance with results obtained by Moysan et al. [11] who reported that hydrogen plateau pressures increase with the increasing Pt concentration in Pd and the fraction of hydride transformed ($\alpha \rightarrow \beta$) diminishes with the addition of Pt in relation to Pd.

4. Conclusions

$Pd_{0.97}Al_{0.03}$, $Pd_{0.9}Pt_{0.1}$ and $(Pd_{0.9}Pt_{0.1})_{0.97}Al_{0.03}$ alloys, before and after internal oxidation, were submitted to hydrogen permeation tests. For the samples without internal oxidation, cold work and the addition of Pt and Al are effective in reducing the apparent hydrogen diffusion coefficient. The reduction of hydrogen diffusion coefficient is more pronounced for the internally oxidized $Pd_{0.97}Al_{0.03}$ alloy where the oxidation produces prismatic nano-precipitates of Al_2O_3.

Pt addition in Pd, inhibits hydride formation in the internally oxidized $(Pd_{0.9}Pt_{0.1})_{0.97}Al_{0.03}$. In internally oxidized $Pd_{0.97}Al_{0.03}$ the hydrogen permeation curve, applying 20 mA, exhibits a double sigmoidal shape indicating hydride formation during the test.

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