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Hydrogenation and X-ray diffraction study of microstresses in Pd alloys

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Received 25 February 1994

Abstract

X-ray diffraction profiles from different concentrations of Pd, Pd–Pt, Pd–Cu, Pd–Sm, Pd–Ru and Pd–Hf alloys have been recorded for cold-worked, annealed and hydrogenated states. Using the peak shift, the relationship between the values of microstresses and the concentrations of added elements as well as the values of $r_{Pd} - r_{ad}$ have been observed.

Keywords: Hydrogenation; X-ray diffraction; Microstresses; Palladium

1. Introduction

In order to use palladium alloys as hydrogen diffusion membranes for purification and isotope separation, the area of the α – β miscibility gap in the hydrogenated alloys should be avoided. The large volume difference between the two phases produces unacceptably high dislocation densities for the α – β cycled alloys [1].

The same difficulty causes the expansion of the palladium lattice due to the rare earth solutes [2].

However, the effect of the magnitude of the palladium lattice expansion, and corresponding stresses, due to the size differences among the components is not necessarily clear.

The purpose of the present study is to obtain more detailed information about the values of microstresses in Pd–Me alloys in and out of the α – β miscibility gap.

The peak shift of X-ray diffraction lines is a very important indicator of alteration in the metal microstructure. If there are no faults (or the concentration is too small), the peak position is sufficient to describe the crystal and lattice parameters. If the concentration of faults is high, the structure peaks have to be displaced from their correct positions. This information can be used to find the type and concentration of faults and other microcharacteristics.

Peak shifts can be caused by a change in the lattice parameters, by microstresses and by the presence of

intrinsic and extrinsic stacking faults. The change in the lattice parameter can be described from two aspects: microscopic and macroscopic. Krivoglas [3] discusses the first position. In his theoretical discussion he describes simple cases of the presence of faults. The orientation dependence of the peak displacement occurs in deformed crystals in which the diffraction maximum is formed in small deformed areas having a lower symmetry than the whole crystal.

2. Experimental procedure and method of analysis

Series of Pd specimens in the solid solution range with 5 and 10 at.% Pt, Cu, Hf, 6 at.% Ru and different Sm contents were prepared, using pure (99.98%) metals. The alloys were then homogenized for 48 h at 900 °C at a pressure of 10^{-6} Torr. The specimens were disc shaped with a thickness of 7 mm and diameter of 16–18 mm. Homogenized discs were cut into two parts. Cold working on all alloy compositions has been achieved by careful hand filing at room temperature. Some of the specimens were annealed at 400 °C for 4 h and water quenched. Hydrogenation of the alloys was performed electrolytically at room temperatures in a solution containing 4 at.% NaF. The anode was a platinum sheet and cathodic current densities of 40 and 80 mA cm^{-2} was used. The X-ray measurements were carried out at room temperatures using Cu $K\alpha$ radiation.

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3. Microstresses and stacking fault probability

The lattice parameters were refined using the $\cos^2\theta$ extrapolation function. The accuracy of the lattice parameter determination was $\pm 0.002 \text{ \AA}$. The presence of stacking faults was indicated using the method described in [4]. If the effect of the presence of stacking and the effect of microstresses are commensurable, it is necessary to include the presence of the first only in the case of high concentrations ($\alpha > 0.01$) and not high microstresses (40 kg mm^{-2}).

In general, the peak shift or corresponding fractional change in the spacing of (hkl) planes should be expressed by [5]

$$\left(\frac{\Delta d}{d}\right)_{hkl} = \epsilon_{hkl} + \alpha(G_{hkl} + J_{hkl}\epsilon)$$

$$\epsilon_{hkl} = \sigma_L \left(\frac{c_{11} + 4c_{12} - 2c_{44}}{4(c_{11} + c_{12})(c_{11} - c_{12} + 3c_{44})} + \frac{1}{2}s_{12} + \frac{1}{2}(s_{11} - s_{12} - \frac{1}{2}s_{44})Y \right)$$

$$Y = \frac{h^2k^2 + k^2l^2 + h^2l^2}{(h^2 + k^2 + l^2)^2}$$

where σ_L is the stress parallel to specimen axis, c_{ij} and s_{ij} are the elastic constants and ϵ_{hkl} is the component of the hkl direction.

In the case when $\alpha = 0$, $\sigma = \text{constant}$ and $\epsilon = \text{constant}$, we can use the equation

$$a_{hkl} = a_0 + \sigma a_0 K_{hkl}$$

where

$$K = \frac{1}{2}(K^{\sigma=\text{constant}} + K^{\epsilon=\text{constant}})$$

$$K^{\sigma=\text{constant}} = \frac{1}{2}s_{12} + \frac{1}{2}(s_{11} - s_{12} - \frac{1}{2}s_{44})Y$$

$$K^{\epsilon=\text{constant}} = \frac{c_{11} + 4c_{12} - 2c_{44}}{4(c_{11} + c_{12})(c_{11} - c_{12} + 3c_{44})}$$

4. Results and discussion

In Fig. 1 we have a typical case of Pd–15at.%Cu deformed specimens [6]. There is a lattice parameter line approximation only in the case of annealed specimens. For deformed specimens it is a zigzag line. The dotted line shows the annealed lattice parameter. As a function of solute contents, the zigzag line moves away at a variable distance from the dotted line. For Pd–15at.%Cu the displacement is the greatest, and for pure Pd the least.

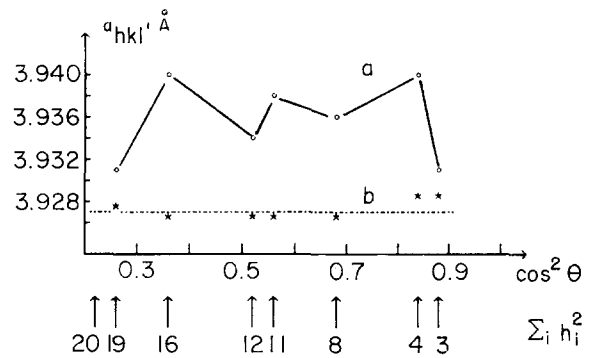


Fig. 1. Lattice parameter for both cold-worked (curve a) and annealed (curve b) states of Pd–15at.%Cu specimens as a function of $\cos^2\theta$ (Nelson–Riley extrapolation function).

In all specimens after hydrogenation the X-ray analysis shows the presence of β phase. The shifted peaks are on the opposite side in α -phase hydrogenated specimens compared with the deformed hydrogen free state. The relation between a and h_i^2 is not very distinct for the β phase. For most of the specimens $a_{111}^\beta < a_{200}^\beta$ is true. We have the same appearance in Pd–10at.%Hf, Pd–15at.%Hf and Pd–6at.%Ru specimens. After hydrogenation of one of these, the zigzag line becomes straight and moves to the area of a lower lattice parameter value.

The specimen containing 15 at.%Hf has been hydrogenated using 40 mA cm^{-2} current density for 60 min (the β phase was not formed). Hydrogenation had an immediate effect on the lattice parameter value in all directions; the distinctions between them become less.

No microstresses in annealed Pd, Pd–Cu and Pd–Pt specimens are observed at the starting positions. In the deformed specimens, the microstresses have negative signs. As a result of hydrogenation we have β -phase formation and a change in the signs of microstresses. a_0^{an} for the α phase generated in annealed specimens have the same signs of the microstresses as the deformed free hydrogen specimens have but the magnitudes are lower. The fact that $a_0^\alpha > a_0^{\text{an}}$ is of significance, too. The signs of microstresses are negative in the β phases generated. For both Pd–5at.%Pt and Pd–15at.%Pt, $\sigma_{\text{def}} < 0$, $\sigma_{\text{an}} = 0$, is true. However, for both (deformed and annealed) specimens, microstresses are positive in their α phases.

The same alterations take place in Pd–Cu specimens after hydrogenation. Negative microstresses with a very high value appear in deformed Pd–15at.%Cu specimens. The subordination of the added concentration is more appreciable for the α phase of deformed specimens. In the β phase, negative microstresses arise weakly compared within the α phase.

The lattice parameter a_0^α for all specimens is greater than a_0^{an} . Table 1 shows the magnitudes of $a_0 - a_{\text{an}}$ for Pd–Cu and Pd–Pt alloys as functions of Cu and Pt

Table 1
Magnitudes of $a_0 - a_n$ for Pd–Cu and Pd–Pt alloys as functions of Cu and Pt contents

Added element	Amount (at.%)	$a_0 - a_n$ (Å)
Cu	0	5×10^{-3}
Cu	5	10×10^{-3}
Cu	10	30×10^{-3}
Pt	0	5×10^{-3}
Pt	5	10×10^{-3}
Pt	10	10×10^{-3}

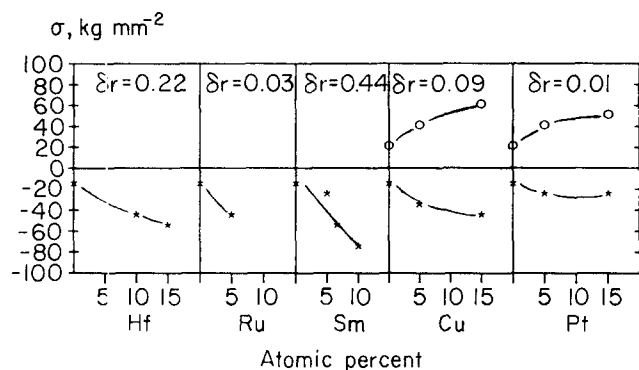


Fig. 2. Microstresses magnitudes in cold-worked palladium alloys (negative) and in their α phases after hydrogenation (positive) as a function of added elements and $\delta r = r_{Pd} - r_{ad}$.

content. It is clear that, after deformation, homogeneous strains arise in the specimens. The value increases with increase in the Cu concentration and remains the same with increase in the Pt content.

The specimens with 15 at.% Hf have negative stresses after deformation. As expected, the stresses decrease and become zero after annealing and increase again after deformation once more (keeping a negative value).

Both specimens containing 10 at.% Hf have equal values of microstresses at the initial stage. By annealing one of them, the microstresses decreased and the same alterations occurred in the second specimen after hydrogenation. We have observed a continuation of the process in the first specimen after 3000 h (keeping it at room temperature) and in the second 500 h after hydrogenation.

Microstresses have been found in all deformed specimens containing Sm. Their magnitudes are a function of Sm concentration and the signs are negative. It is important to point out that phase transformations take place together with hydrogenation [7,8]. After hydrogenation of the specimens containing 8.2 at.% Sm (15 min at 40 mA cm^{-2}) the microstresses decrease but keeping the same signs; later (in the gas-free state) they increase again and go back to the starting state. The situation is repeated with increasing charging time,

but doubling the current density we achieve a change in the signs of the stresses.

Fig. 2 shows the microstress magnitudes in cold-worked palladium alloys (negative) and in their α phases after hydrogenation (positive) as a function of added elements and $\delta r = r_{Pd} - r_{ad}$. The values of the microstresses in both cases increase with the increasing added concentration; furthermore, their magnitudes correlate with $r_{Pd} - r_{ad}$.

We found differences between microstresses in α phases of deformed and annealed specimens. In pure palladium and alloys with low Cu and Pt contents, the microstresses increase more slowly in annealed than in deformed specimens. As the concentration of the added metal increases, this difference disappears. We also found that the sign of the microstresses is reversed only in the case of a transition to the critical parameters charging time and current density. If not, the microstresses are restored to their initial signs but the values become lower.

It is known that annealing brings the system to equilibrium. Hydrogenation transforms it to a new state with a high energy of deformation. This could be the reason for faults arising and microstress alterations.

5. Conclusions

- (1) In all the alloys examined, there exist microstresses, which grow on increase in added element concentration and reach certain values correlating with the magnitudes of $r_{Pd} - r_{ad}$.
- (2) Hydrogenation reduces the microstresses; they pass through zero, changing sign when the critical parameters j and t are reached.
- (3) We found the same microstress behaviour with added element concentration and $r_{Pd} - r_{ad}$ magnitude in α phases as we had in cold-worked specimens.

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