MEMBRANE CHARACTERISTICS OF PALLADIUM-SAMARIUM ALLOY FOILS: MECHANICAL PROPERTIES AND HYDROGEN PERMEABILITY

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Abstract

Palladium membranes have a high selectivity for hydrogen, which is coupled with their temperature and mechanical stability. Such a selectivity of palladium membranes makes the membrane method the single procedure that allows one to prepare the high-purity hydrogen (no less than 99.9999 vol%) being the main energy carrier in hydrogen power engineering. Palladium-rare earth metal solid solutions are possible hydrogen diffusion membrane alloys, since they exhibit the mechanical stability during the permeation along with the high hydrogen permeability characteristic. Palladium-samarium alloys of nominal compositions Pd-2.6, 3.2, 5.2, 6.8, 8.3, 9.5, and 11 at% Sm were prepared by arc melting; ingots were subjected to free forging and cold rolling to a thickness of 50 μm with intermediate annealing. Vickers hardness, ultimate tensile strength, and relative elongation, were determined and the hydrogen permeability was measured. Within the solid-solution compositions, the strengthening takes place; the ultimate strength increases from 200 MPa (for Pd) to 830 MPa for Pd-8.3 at% Sm. In this case, the relative elongation remains close to that of pure Pd (21 %). Such mechanical characteristics favor the manufacturing ultrathin foils and show promise for using them in high-performance membranes and membrane elements. The alloys demonstrate the high hydrogen permeability at 300 – 600 K, which is higher substantially as compared to that of Pd alloys alloyed with other elements. Variations of mechanical properties and hydrogen permeability are discussed from the viewpoint of the possible ordering of the solid solutions and formation of hydride phases.

Keywords: Palladium-samarium alloys, solid solution, foil, hydrogen permeability, mechanical properties

1. INTRODUCTION

Industrial application of palladium membranes can result in significant advance in the separation of hydrogen from gas mixtures and in the development of innovative applications of palladium alloys. Palladium membranes have a high selectivity for hydrogen, which is coupled with their temperature and mechanical stability. Such a selectivity of palladium membranes makes the membrane method the single procedure that allows one to prepare the high-purity hydrogen (no less than 99.9999 vol%) being the main energy carrier in hydrogen power engineering.

The disadvantage of palladium membranes, which limits their large-scale application, consists in the medium hydrogen permeability and high cost. The lowering the palladium membrane thickness, still preserving the mechanical strength, would addressed the problems of membranes for the hydrogen separation. For this reason, the attention of investigators is focused on the search for components for the alloying of palladium, which allow one to increase its hydrogen permeability and to ensure the adequate mechanical strength and plasticity for manufacturing thin foils from the alloyed palladium-based compositions.

It was shown [1] that palladium-rare earth metal (REM) solid solutions are possible hydrogen diffusion membrane alloys, especially because the alloys containing about 8 at% Y exhibit the mechanical stability during the permeation along with the high hydrogen permeability characteristic. The composition with 8 at% is the critical composition for the disappearance of the hydrogen miscibility gap in the Pd-Y-H system. The closure of the miscibility gap is one the main factors controlling the hydrogen solubility in palladium-REM alloys and takes place at an electron-to-atom (e/a) ratio of 0.24.

The maximum solid solubility of REMs in palladium is anomalously high. The expansion of the palladium lattice due to the REM solubility is great [2]. Therefore, there is significant solid solution hardening in these alloys and, thus, the possibility of manufacturing a stronger membrane material.

Unlike the traditional Pd-Y alloys that are well understood from the viewpoint of interaction with hydrogen, the Pd-Sm compositions were studied only in a few works, in particular, in [2] and [3].

According to the Pd-Sm phase diagram [4], the samarium solubility in palladium is 10.38 at% at 1351 K (the eutectic temperature). As the temperature decreases, the Sm solubility decreases. The region of limiting Sm solubility in Pd-Sm alloys corresponds to the short-range ordered Pd_7Sm phase (12.5 at% Sm), which coexists with the fcc Sm solid solution in Pd (substitutional solid solutions with the Cu-type structure, space group *Fm-3m*). The formation of the ordered phase is accompanied by a peritectoid reaction: α-Pd + Pd_5Sm (16.7 at% Sm) at 547 °C (in contrast to the other Pd-REM systems, in which the reaction α-Pd + Pd_3Sm takes place).

The lattice parameter of palladium increases almost linearly with increasing Sm content [2]. The magnitude of the palladium lattice expansion due to addition of Sm, $\Delta a_{ss}/\Delta x_u$ (where x_u is the solute atomic fraction), which determines the hydrogen diffusion, is higher than that for Y. However, contrary to expectation, the lattice expansion of the Pd-Sm is slightly smaller when compared with the tendency of the other rare earth metals and their atomic number [2].

The aim of the present work is to prepare Pd-Sm alloys with from 2.6 to 11 at% Sm in the form of foils 50 μm thick and to study regularities of variations of their mechanical properties and hydrogen permeability at different temperatures.

2.   EXPERIMENTAL

Palladium-samarium alloys of nominal compositions Pd - 2.6, 3.2, 5.2, 6.8, 8.3, 9.5, and 11 at% Sm were prepared by arc melting using Pd of 99.95 wt% purity and distilled samarium 99.9 wt% purity. The melting was performed in a purified argon atmosphere using a water-cooled bottom and nonconsumable tungsten electrode. The chemical compositions of alloys were determined by X-ray fluorescent analysis using a VRA-33 spectrometer (Carl Zeiss, Germany).

After a homogenizing annealing at 1223 K for 5 h in a vacuum, the rectangular ingots were subjected to free forging and cold rolling to a thickness of 50 μm (using Duo and Quarto mills) with an intermediate annealing. Finally, the foils were annealed at 1123 K for 1 h in a vacuum and subjected to furnace cooling.

The Vickers hardness of the foils was studied using a 401/402-MVD hardness tester (Instron Wolpert Wilson Instruments). The mechanical characteristics, ultimate tensile strength and relative elongation of the foils in the annealed state were determined using an Instron 3382 testing machine.

The hydrogen permeability was measured by filling a calibrated volume using an original experimental set up equipped with a high-temperature cell. The diameter of operating membrane surface is 20 mm; the range of operating temperatures is 340-923 K. The range of operating pressures before and after the membrane can vary from 0.1 to 2.5 MPa and from 0.02 to 1.0 MPa, respectively.

Using results of measurements, the specific hydrogen permeability was calculated for a membrane 1 mm thick for each of measuring temperatures by the expression:

$$Q = \frac{\Delta P \cdot V_\kappa \cdot T_0 \cdot s}{T_1 \cdot p_0 \cdot F \cdot \tau(\sqrt{p_{ent}} - \sqrt{p_{ex}})};$$

(1)

where

V_k - the calibrated volume (m^3); Δp - the pressure difference in the calibrated volume when filling the sell with hydrogen (MPa); $T_0 = 273$ K; s - the membrane thickness (mm); T_1 - the ambient temperature (K); $p_0 = 0.1$ MPa; S - the area of operating membrane surface (m^2); τ - the time of calibrated volume filling (h); p_{ent} - the pressure before the membrane (MPa); p_{ex} - the pressure after membrane (MPa).

3.   RESULTS

3.1.   Mechanical properties

The hardness (**Figure 1**), ultimate tensile strength, and relative elongation (**Figure 2**) of 50 µm foils were measured in accordance with their composition.
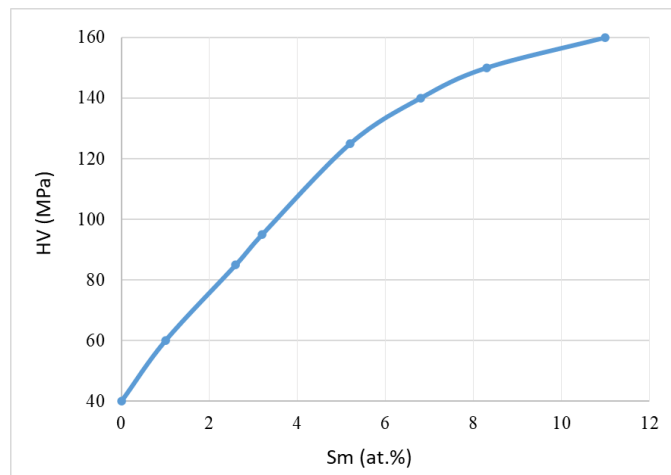

Figure 1 Composition dependence of the Vickers hardness of the Pd-Sm foils 50 µm in thickness
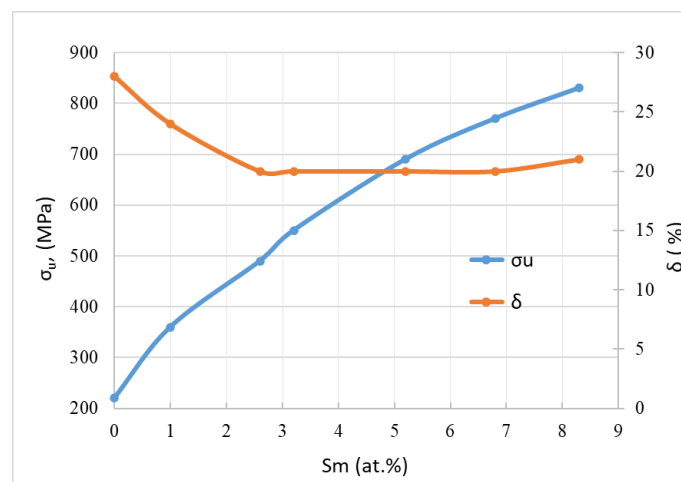

Figure 2 Ultimate tensile strength (σ_u) and relative elongation (δ) of Pd-Sm foils 50 µm in thickness

It is seen that the hardness of the foils increases monotonically from 400 MPa (pure palladium) to 1600 MPa for the Pd-11 at% Sm composition. The ultimate strength σ_u for palladium is 200 MPa. The Pd-8.3 at% Sm foil

exhibits an ultimate strength of 830 MPa; in this case, the relative elongation of Sm solid solutions is sufficiently high, namely, δ = 21 % for the Pd-8.3 at% Sm composition.

The hardness measurements allow us to estimate the effect of Sm on the strengthening of palladium. As is known [5], the solid solution hardening is due to the atomic size misfit. The studied foils correspond to the fcc Pd-based solid solution. The lattice parameter of the solution varies linearly with composition up to 8 at% [2]. In [5], the common feature of the compositional dependences of the hardness of a number of REM solid solutions in palladium is a marked decrease in rate of the hardness increase with increasing the REM concentration, which is observed around the middle of the solid solution range.

The analysis of the compositional dependence of the hardness (**Figure 1**) of Pd-Sm alloys allows us to divide the curve into two portions. The first portion includes a range of 0 to ~5 at% Sm and is characterized by the abrupt increase in the hardness. The composition with 5 at% Sm corresponds to the middle of the solid solution range. The further increase in the Sm content results in the decrease in the increment in the hardness per atomic percentage of samarium. It should be noted that, according to the Pd-Sm phase diagram [4], at room temperature, the Sm solubility in Pd does not exceed ~4 at% Sm. At the higher Sm contents, the Sm solid solution is in equilibrium with the Pd_7Sm compound.

It is obvious that the hardness variations are due to changes in the solid solution lattice, namely, the transition from a disordered to a short-range ordered (SRO) solid solution with increasing samarium content. The palladium-rare-earth solid solutions are ideal candidates for the appearance of SRO since there are very significant differences in both the atomic sizes and the electronegativities of the component atoms [5]. Since the Sm solid solution is in equilibrium with Pd_7Sm compound, the SRO is assumed to be based on the Pd_7Sm superlattice [4]. The variations of the hardness with increasing Sm content can be explained based on assumptions available in [5], namely, in terms of a rapid increase of the strain energy for more disordered solid solutions, and the subsequent relief of this increase in strain energy with composition by the appearance of extensive SRO at higher Sm contents.

According to [3], Pd-Sm alloys in the composition range between 5.0 and 15.0 at% Sm indicate the presence of an ordered phase in the form of a Pd_7Sm superlattice. However, the dependence of the ultimate tensile strength of Pd-Sm alloys is characterized by monotonic increase in σ_u with increasing Sm content and exhibits no anomalies. According to [6], the large strengthening effect is high for light rare-earth elements and is medium for Sm; there is a linear relationship between the tensile strength and the rare-earth metal concentration which is valid for dilute concentration up to 0.6 at% REM. According to the data, the increase in the tensile strength of the solid solution is 33 MPa per 0.1 at% Sm. Our results agree with the literature data. The concentration dependence of the relative elongation exhibits first the decrease in δ up to 2.5 % Sm as compared to that of Pd and, after that, the relative elongation remains almost unchanged.

3.2. Hydrogen permeability

In the palladium-hydrogen system two fcc phases, designated α and β with low and high concentrations of hydrogen, respectively, can co-exist at room temperature over a range of hydrogen contents (α and β which may be termed the α/β miscibility gap) [7]. The alloying with REMs suppresses the formation of β phase and it was found that, under operating conditions, a continuous metal-hydrogen phase (α) could be guaranteed for palladium alloys containing 8 at% REM (6.5 % Ce) [1].

Figures 3 and **4** show the temperature and composition dependences of the hydrogen permeability of Sm-Pd alloys, respectively.

The variations of the hydrogen permeability (**Figure 3**), which are characterized by a maximum and observed for the compositions with to 6.8 at% Sm, are related to the existence of α/β miscibility gap in the alloys. For the compositions with more than 8 at% Sm, no maximum in the dependence is observed.

As it was mentioned above, the hydrogen permeability is greatly increased by the presence of the short-range ordered phase [2]; the diffusivity of hydrogen in the ordered alloys is much greater than in the disordered state, but the ordered alloys dissolve less hydrogen than do the disordered alloys. In the case of Pd-Sm system, the ordered phase Pd_7Sm appears in the compositions with more than ~ 5 at% Sm, and the hydrogen permeability of the alloy with 5.2 at% begins to increase (**Figure 4**). Its increase becomes more substantial for the compositions with more than 8 at% Sm. For the compositions with more than 10 at% Sm, the presence of the Pd_5Sm ordered phase is possible [4].
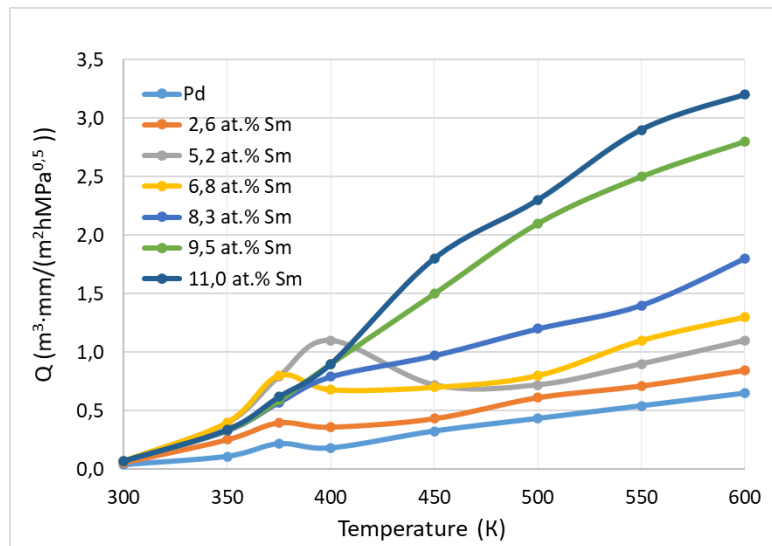

Figure 3 Temperature dependences of the hydrogen permeability of Pd-Sm foil alloys
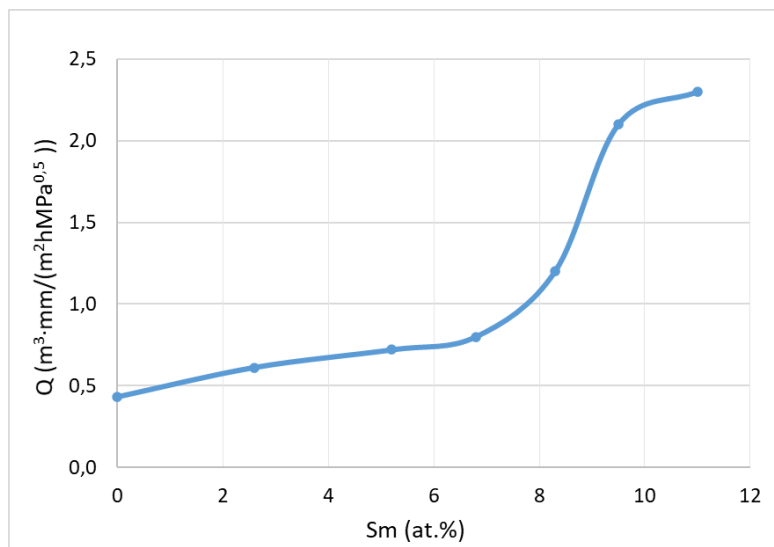

Figure 4 Composition dependence of the hydrogen permeability of Pd-Sm foil alloys at 523 K

The hydrogen permeability of Pd-Sm alloys at low temperatures (to 550 K) is higher substantially than that of Pd (1.5-2 times).

It should be noted that, according to [2] Pd-Sm alloys seem to be better candidates for use as hydrogen purification membranes (as compared to Pd membranes) because these alloys have a larger lattice expansion at the critical composition (corresponding to the disappearance of the β phase), and large lattice expansion is, in general, favorable for hydrogen diffusion.

4. CONCLUSION

The Pd-Sm foils 50 μm in thickness with Sm contents of 2.6, 3.2, 5.2, 6.8, 8.3, 9.5, and 11 at% were prepared by cold rolling. The hardness, ultimate tensile strength, and relative elongation of the foil alloys were studied. The substantial solid solution strengthening was demonstrated; the relative elongation remains close to that of pure Pd (21 %). Such mechanical characteristics favor the manufacturing ultrathin foils and show promise for using them in high-performance membranes and membrane elements.

The Pd-Sm alloys demonstrate the high hydrogen permeability at moderate temperatures (to 600 K), which is higher substantially as compared to that of Pd-based compositions alloyed with other elements. This fact determines the possibility of using the Pd-Sm membrane in performing low-temperature catalytic processes.

Variations of mechanical properties and hydrogen permeability are discussed from the viewpoint of the possible ordering of the solid solutions (Pd_7Sm superlattice) and formation of hydride phases.

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