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Palladium-rare-earth metal alloys-advanced materials for hydrogen power engineering

Burkhanov G. S., Roshan N. R., Kol'chugina N. B., Korenovskii N. L.

(Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, Moscow 119991, Russia)

Abstract: Hydrogen of no less than 99.999% (vol. fraction) purity is a principal power media of hydrogen power engineering. A single method for the preparation of high purity hydrogen consists in its separation from vapour-gas mixtures via the selective diffusion of hydrogen through a palladium membrane. The rate of hydrogen diffusion and the strength and stability during the operation in aggressive gases are important characteristics of palladium membranes. The increase in the strength, plasticity, and hydrogen-permeability of membrane alloys can be reached by alloying palladium with the formation of solid solutions.

The formation of wide ranges of palladium-rare-earth metal (REM) solid solutions is an interesting feature of palladium. Earlier, we have shown that the alloying of Pd with REM substantially increases the rate of hydrogen diffusion and markedly increases the strength of palladium on retention of the adequate plasticity.

In this work, we have studied alloys of the Pd-Y and Pd-Y-Me systems. It was shown that the following conditions should be satisfied to prepare high-quality alloys exhibiting high service properties: (1) the use of high-purity components (whose purity is no less than 99.95%, mass fraction), in particular, high-purity Y prepared by vacuum distillation, and (2) holding the reached purity for the final product. For this purpose, we suggested a cycle of manufacturing operations including the preparation of a vacuum-tight foil of 50 (m thick as the final stage.

The hydrogen-permeability of the alloys was measured at different temperatures and hydrogen pressures. The instability of operation of binary Pd-Y alloys w alloying the composition with a VIII Group metal. For example, the alloy of the optimum composition Pd-8Y-Me in the annealed state exhibits the following mechanical properties: HV=75 kg/mm^2, σ_u=58 kg/mm^2, and δ=20%. Its hydrogen-permeability (Q_{H2}) measured as a function of the temperature exceeds that of the Pd-23Ag alloy (that is widely used by foreign companies) by a factor of 1.5-2; it is 3.6-4.7 $m^3/m^2hMPa^{0.5}$ at 300-600℃, respectively.

The alloys exhibiting the high hydrogen-permeability combined with the high mechanical properties shows promise as materials for diffusion hydrogen purification devices whose productivity reaches tens thousands nm^3/h.

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1 Introduction

Hydrogen of no less than 99.999% (vol. fraction) purity is a principal power media ofor hydrogen

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power engineering. A single method for the preparation of high purity hydrogen consists in its separation from vapour-gas mixtures via the selective diffusion of hydrogen through a palladium membrane. The rate of hydrogen diffusion and the strength and stability during the operation in aggressive gases are important characteristics of palladium membranes. The presence of hydride phases and their mutual transformations lead to the failure of diffusion membranes made of pure (non-alloyed) palladium after several "heating-cooling" cycles in a hydrogen atmosphere. Because of this, the problem of the development of strength palladium-based alloys whose hydrogen-permeability is higher than that of pure palladium is of high-priority task. Moreover, membranes comprise foils of a micron-sized thick; because of this, the alloys intended for these membranes should exhibit, along with the high hydrogen permeability, the high mechanical both strength and plasticity, i. e. , should correspond to the Pd-based solid-solution range.

The increase in the strength, plasticity, and hydrogen-permeability of membrane alloys can be reached by alloying palladium within a solid solution range.

The formation of wide ranges of palladium-rare-earth metal (REM) solid solutions with all rare-earth metals (to 10%-15%, mass fraction), except La and Nd (to 2%, mass fraction), is an interesting feature of palladium in spite of the fact that factors determining the rare-earth metal-palladium interaction are unfavourable.

Earlier, we have studied Pd-based alloys containing La or Nd to 2% (mass fraction) and Sm or Lu to 15%. It was shown that the alloying of Pd with a rare-earth metal additions increases substantially the rate of hydrogen mobility and increases substantially the strength of palladium on retention of the adequate plasticity. For example, the ultimate strength of palladium alloyed with 7%-9% (mass fraction) Lu or Sm is higher than that of pure palladium by a factor of 3; in this case, the plasticity of alloyed palladium exhibits only 10% decrease.

The alloys Pd-8%Lu (mass fraction) and Pd-12%Sm (mass fraction) exhibited the highest rate of hydrogen mobility at 300℃. However the alloying with Sm increases markedly the oxidation ability of Pd, whereas Lu exhibiting the higher corrosion resistance is a very expensive metal[1].

A number of works reporting about the high hydrogen permeability of palladium-yttrium alloys (the optimum compositions is Pd-7% Y (mass fraction) is available in the literature. The origin of the phenomenon is not explained.

Because of this, the study of Pd-Y system alloys in the range of solid solutions is of practical and theoretical interest.

2 Results and discussion

The phase diagram of the Pd-Y system is rather complex (Fig. 1). It is characterized by the formation of seven intermetallic compounds. The maximum solubility of yttrium in palladium at 1200℃ (the eutectic temperature) is about 12%(mass fraction). Palladium is virtually insoluble in yttrium.

Since palladium-rare-earth metal alloys exhibit the capability to oxidation and formation of complex impurity inclusions in the crystal lattice, the chemical purity of initial components, in particular rare-earth metals, and the possibility of the purity holding (during the preparation) for the final product play an important role for the preparation of high-quality alloys and then thin foils.

As starting materials, we used palladium of 99.95%(mass fraction) purity and yttrium purified by twofolddouble vacuum distillation to 99.893%(mass fraction) purity.

The vacuum distillation of yttrium was performed in a resistor furnace with a graphite heater. In this

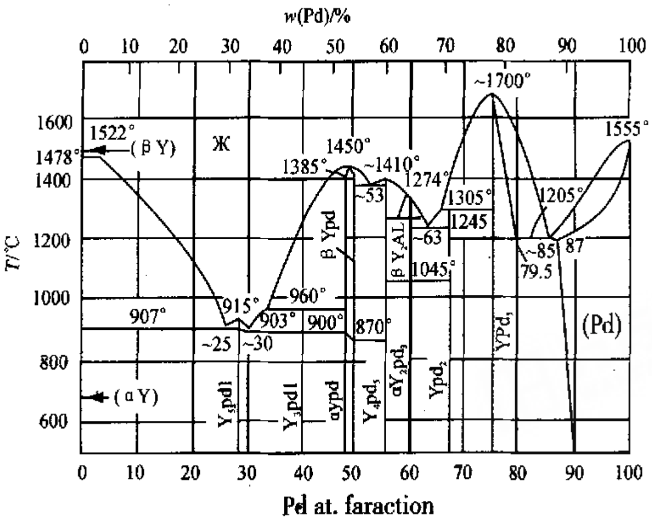

Fig. 1 Phase diagram of the Pd-Y system.

process, the metal was evaporated from a tantalum crucible at a temperature of 50-250℃ higher than its melting point. The evaporation is realized for 10 h in a vacuum of 2×10^{-6} Torr[3]. The pure metal is deposited on a copper water-cooled condenser in the form a druse of together-growing crystals. The process results in a substantial decrease in metallic and, in particular, interstitial impurities. Starting and distilled yttrium was analyzed by spark mass spectrometry for 70 elements.

The Pd-based alloys were prepared by arc melting in a purified helium atmosphere (under an excess pressure) using a non-consumable tungsten electrode and a water-cooled bottom.

We prepared palladium-based alloys containing 6%, 8%, and 10% (mass fraction)Y as well as alloys Pd-6%Y-0.5%Me_{VIII}(mass fraction) and Pd-8%Y-0.5%Me_{VIII}(mass fraction). A metal of Group VIII of the Periodic Table was used as a stabilizing addition. The weight of ingots is equal to 30 g. To reach the uniform composition of the alloys, the ingots were melted twice. The composition of alloys was studied by chemical analysis. Plane blanks 180g in weight for the subsequent rolling to foils were melted using the aforementioned ingots, the arc furnace, and a water-cooled bottom designed at the Baikov Institute of Metallurgy and Materials Science, RAS.

The plane blanks were subjected to hammering at a total reduction of area of 50%-75% to 3-4 mm thick (depending on the alloy composition) and subsequent vacuum annealing (the vacuum is higher than 10^{-4}mmHg) at 900℃ for 30-90 min (depending on the plate thickness). A foil 50 (m in thickness was produced by 7 passes.

We measured the mechanical properties and hydrogen permeability for all of the alloys. The hardness of (H_V) of the annealed (in vacuum at 900℃ for 3 h) alloys is equal toranged from 65 andto 85 kg/mm^2 for Pd-6%Y and Pd-10%Y (mass fraction), respectively.

Before the measuring of the hydrogen permeability, the foils were tested for the tightness using diffusions cells.

The hydrogen permeability was measured using an original equipment-test bed including a volumetric measuring cell with a foil membrane made of a palladium-based alloy as a principal element [4]. The diameter of operating surface of the membrane is 20 mm.

Table1 shows the specific hydrogen permeability of the different alloys measured at different temperatures. Figure 2 shows the plotted temperature dependences for the alloys.

Table 1 Specific hydrogen permeability Q_{H2} (m^3/m^2 h $MPa^{0.5}$) of the Pd-based alloys measured at different temperatures

N	Alloy composition	Temperature/℃					
		350	400	450	500	550	600
1	Pd-6%Y	4.8	4.9	5.0	5.2	5.5	5.8
2	Pd-8%Y	3.3	3.8	4.0	4.1	4.2	4.3
3	Pd-10%Y	2.5	3.0	3.3	3.7	3.8	4.0
4	Pd-6%Y-0.5Me	3.1	3.2	3.4	3.7	3.8	3.9
5	Pd-8%Y-0.5Me	3.6	4.0	4.3	4.4	4.5	4.7
6	Pd-6%In-0.5Ru	1.0	1.2	1.5	1.7	1.9	2.2
7	Pd-23%Ag	1.6	1.9	2.3	2.9	3.0	3.4

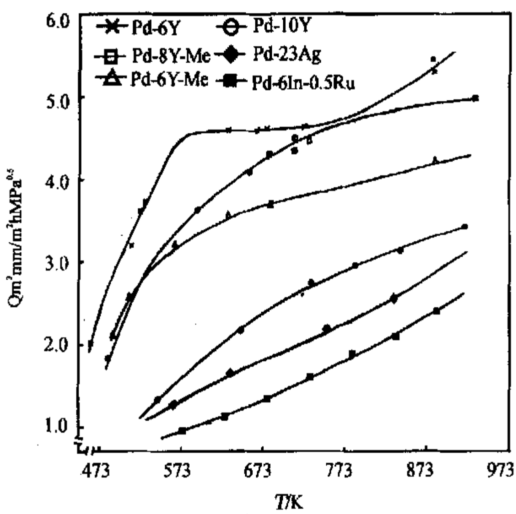

Fig. 2 Temperature dependences of the specific hydrogen permeability of different Pd-based alloys

3 Conclusions

The hydrogen permeability of palladium-yttrium alloys as a function of the temperature was found to exceed that of widely used (in other countries) Pd-23%Ag and the Pd-6%In-0.5%Ru alloys by a factor of 2-3. The unstable operation of the binary Pd-Y alloys in hydrogen atmosphere was corrected using Me_{VIII} alloying.

For example, the alloy of the optimum composition Pd-8Y-Me in the annealed state exhibits the following mechanical properties: HV = 75 kg/mm^2, σ_u = 58 kg/mm^2, and δ = 20%. Its specific hydrogen permeability (Q_{H2}) measured as a function of the temperature is 3.6-4.7 $m^3/m^2hMPa^{0.5}$ at 300-600℃.

The Pd-Y-Me alloys exhibiting the high hydrogen permeability combined with the high mechanical properties show promise as materials for diffusion hydrogen purification devices whose productivity reaches tens thousands m^3/h.

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