Development of methods of creation metal hydrogen permeation films

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Abstract. The application of electrothermal and magnetron sputtering methods for manufacturing thin films containing palladium and silver is investigated. In the process of electrothermal sputtering, indirect heating of the evaporated material was used in a tungsten and tantalum boat, through which a current has been conducted and a direct heating of a thin plate of palladium alloy has been entailed by current. A composite target for magnetron sputtering of alloys using silver and palladium plates with different ratios of their areas has been developed. The dependence of the film composition on the target composition is determined. As a result of sputtering for 40 min, a sample with a thickness of 1.1 microns and a silver content of 23.2±0.7% was obtained from a target with an area ratio S(Ag)/S(Pd) = 20.8/79.2.

1. Introduction

Palladium-containing membranes are used in the hydrogen release from gas mixtures to produce high-purity hydrogen [1-3] and also in the processes of hydrogen isotopes separation [4,5]. The main characteristics of palladium membranes for the hydrogen separation from gas mixtures are the rate of hydrogen permeation through the membrane, its strength and durability during exploitation [6,7]. The usage of pure palladium is limited by existing at temperatures below 300°C and a pressure of 2 MPa of α and β hydride phases, whose mutual transformations lead to the destruction of diffusion membranes after several cycles of heating and cooling in a hydrogen atmosphere [8]. Palladium alloys with a number of d- and f-elements are mechanically strong during hydrogen tranfer, while maintaining high solubility and permeability [1,9]. The most well-studied materials for a hydrogen-permeable membrane are palladium-silver alloys, in which the hydrogen permeability changes according to an extreme law and reaches a maximum when the silver content is 15-25 % [10-13]. These alloys have a high hydrogen permeability and they are mechanically stable, which makes it possible to produce thin films (up to 1 microns) [14].

Pd is an expensive metal and its hydrogen permeability is usually inversely proportional to the thickness of the film [15], so it is necessary to maintain a balance between the characteristics of the palladium membrane and its thickness. Palladium membranes produced by cold rolling have a minimum thickness of about 20-25 microns, which is enough to transfer the required amount of hydrogen. Reducing the thickness of the membrane can lead to defects: pores and microcracks, intermetallic diffusion between the substrate and the membrane [16-18]. The gas permeation rate is inversely proportional to the thickness, so methods for producing thin mechanically stable palladium-containing membranes are currently developed.
We propose the usage of a palladium alloy for the preparation of a dense all-metal gas-diffusion hydrogen electrode for a hydrogen-air fuel cell instead of the usually used porous gas-diffusion electrode. The novelty will allow to use a liquid electrolyte in the fuel cell and will lead (by changing the three-phase gas-metal boundary of the current collector-electrolyte to a two-phase palladium alloy-electrolyte) to improve the current-voltage characteristics of the element, reduce polarization, reduce internal resistance, and increase the specific power. In addition, palladium is a catalyst for the electrode process along the entire two-phase boundary, so it does not need additional catalyst application.

The great importance of the production of alloys is the purity of palladium for gas-forming impurities. Palladium is prone to internal oxidation and the formation of complex impurity inclusions in the crystal lattice, so the chemical purity of the initial components and the possibility of preserving the purity in the final product are of great importance for obtaining high-quality alloys, which depends on the method of production the alloys [19]. Palladium alloys obtained by vacuum deposition are clean in terms of impurities and retain good ductility ($\delta>20\%$), which allows produce a foil with a thickness of one micron by cold rolling with intermediate vacuum annealing. Palladium doping affects the diffusion of hydrogen within the membrane, the rate of dissolution and release of hydrogen atoms, recombination and dissociation of molecules, and, to adsorption and desorption (in a lesser extent). As a result of palladium doping, the temperature of the $\alpha\leftrightarrow\beta$ phase hydride transition and the hydrogen permeability coefficient with respect to pure palladium change [20-22].

The base for the development of the hydrogen diffusion filter material has been the palladium-silver alloys, in which the hydrogen permeability changes according to an extreme law and reaches a maximum when the silver content is 15-25%. Concentration dilation and an increase in the volume of the membrane as a result of the dissolution of hydrogen in it, can lead to concentration stresses and depressurization of the membranes. A larger amount of silver in the alloys reduces the purity of the diffused hydrogen and does not allow reducing the dew point below -70°C, and poisons the membrane [19].

2. Methods and materials

2.1. Methods for creating the basis of self-supporting membranes

Palladium was used as raw material for metalworking in the form of refined ingots, geometric dimensions of 20x40x2 mm with a purity of 99.8% (main impurities: platinum, iridium, rhodium (0.02%), silicon, copper (0.01%), iron, Nickel (traces)) and silver in refined ingots, geometric dimensions 30x60x6 mm, purity 99.99%. (main impurities: gold, copper (0.01%), zinc (traces)). Gas impurities in palladium and silver were not determined.

Rough forging for silver was carried out by a wedge-shaped striker on an alloy anvil along the length of the ingot to a forging thickness of 3-3.5 mm with further smoothing with a flat striker to a thickness of 3 mm. The structure was followed by intermediate annealing at 300°C for 20 seconds.

Rolling operations were performed by Durston DRM-130 rollers with an adjustment step of 25 microns. Then the forged silver was rolled from a thickness of 3 mm to a thickness of 1 mm in two operations in perpendicular directions with one intermediate annealing. The final annealing was not performed in order to preserve the hardening for increased hardness of the sprayed metal. A disc for a target with a diameter of D = 57 mm was cut from the resulting rolled metal. After that, the silver disk was perforated according to the method described above.

The palladium ingot was rolled without preliminary forging along the length to a thickness of 1 mm, annealed at a recrystallization temperature of 450°C, then rolled in a perpendicular direction to a thickness of 0.5 mm and then with intermediate annealing and changing the directions of rolling to a thickness of 0.1 mm.

2.2. Methods of creating thin films

Two methods were used to create hydrogen-permeable thin films:

1) The electrothermal sputtering method. The AUTO 500 Edwards unit was used to obtain thin films by electrothermal sputtering. The deposition process was controlled by the pressure in the working
chamber, the amount of electric current evaporator, sputtering time and substrate temperature. Two methods of evaporation of the palladium-containing sample were used:
1. indirect heating of a sample of vaporized material in a tungsten and tantalum boat, through which an electric current was passed;
2. direct heating of a thin plate of palladium alloy by electric current.

(2) The magnetron sputtering method. Experiments on magnetron sputtering of metal samples of thin films of palladium-containing alloys were performed on the Quorum Q150TS/E/ES device. Silver and palladium plates with different ratios of their areas were used as targets for the magnetron. The ratio of free surfaces was controlled by precise measurement of their surface areas.

3. Results and discussion
In the article, we have studied the properties of samples obtained by electro deposition in a variety of ways, differing in the way the material of the evaporator and the substrate material. The obtained results are presented in Table 1.

| Substrate material | The method of spraying, | Substrate temperature, °C | Time, min | Deposition rate, nm min⁻¹ | Film thickness, nm |
|--------------------|-------------------------|---------------------------|-----------|----------------------------|------------------|
| polished silicon   | 1, tungsten, T>Tₘₜₐₜ   | 300                       | 10        | 7.4                        | 74               |
| sitall             | 1, tantalum, 1400<T<Tₘₜₐₜ| 55                        | 50        | 3.9                        | 194              |
| sitall             | 2, palladium, T<Tₘₜₐₜ    | 30                        | 60        | 4.5                        | 272              |
| sitall             | 1, alundum, T<Tₘₜₐₜ     | 50                        | 60        | 3.9                        | 233              |

The thickness of the films was determined using atomic force probe microscopy and refractometry. Figure 1 shows the topography of the surface of the sample obtained by spraying on Sitall.

![Figure 1](image)

**Figure 1.** The topography of the sample surface containing the palladium-silver alloy, electrothermal deposited on Sitall.

Studies of the corrosion resistance have shown the possibility of using materials as an anode during using alkali solutions (up to 20% NaOH) as an electrolyte.

The chemical composition of films obtained by magnetron sputtering has been studied by micro-x-ray spectral analysis on an INCA (Oxford) semiconductor energy-dispersive attachment as part of a JEOL JSM-7500F scanning scanning electron microscope.

To determine the degree of uniformity of the coating, the elemental composition was measured at various locations on the film surface. The results of measurements of the silver and palladium content demonstrate acceptable uniformity of the composition (Table 2).
Table 2. Composition of palladium-silver films obtained by magnetron sputtering.

| Area ratio Ag/Pd | No. of measuring point | The content in the film, % |       |       |
|-----------------|------------------------|---------------------------|-------|-------|
|                 |                        |                           | Ag    | Pd    |
| 8/92            | 1                      | 8.81                      | 91.19 |
|                 | 2                      | 8.51                      | 91.49 |
|                 | 3                      | 9.34                      | 90.66 |
|                 | average                | 8.89                      | 91.11 |
|                 | standard deviation     | 0.42                      | 0.42  |
|                 | 1                      | 17.01                     | 82.99 |
|                 | 2                      | 17.22                     | 82.78 |
| 15/85           | 3                      | 17.65                     | 82.35 |
|                 | average                | 17.29                     | 82.71 |
|                 | standard deviation     | 0.33                      | 0.33  |
|                 | 1                      | 22.95                     | 77.05 |
|                 | 2                      | 23.89                     | 76.11 |
| 20/80           | 3                      | 24.23                     | 75.77 |
|                 | average                | 23.69                     | 76.31 |
|                 | standard deviation     | 0.66                      | 0.66  |
|                 | 1                      | 28.02                     | 71.98 |
|                 | 2                      | 28.74                     | 71.26 |
| 25/75           | 3                      | 29.65                     | 70.35 |
|                 | average                | 28.80                     | 71.20 |
|                 | standard deviation     | 0.82                      | 0.82  |
|                 | 1                      | 41.90                     | 58.10 |
|                 | 2                      | 42.13                     | 57.87 |
| 40/60           | 3                      | 43.20                     | 56.80 |
|                 | average                | 42.41                     | 57.59 |
|                 | standard deviation     | 0.69                      | 0.69  |

The analysis data demonstrate that the composition of the films in general corresponds to the area ratio. With the area ratio, the increase in the silver content in the film relative to its content in the target can be explained by a lower value of the energy required for silver atomization relative to palladium ($\Delta H(\text{Ag}) = 250 \text{ kJ mol}^{-1}$, $\Delta H(\text{Pd}) = 364 \text{ kJ mol}^{-1}$ [23, 24]). Based on experimental data, the graph shown in Figure 2 makes it possible to select the target composition for obtaining films of a given composition.

**Figure 2.** Dependence of the film composition on the target composition.

Therefore, a composite target for magnetron sputtering of metal alloys based on pure metal components has been obtained, which allows sputtering of alloys (for example, Pd – Ag) with an
accuracy of ±0.7%. The advantages of sputtering using such a target are: the possibility of using pure metals – components of the sprayed alloy, and thus, the absence of a rather labor-intensive stage of alloy preparation, as well as a simpler change in the ratio of components in the alloy and easy regeneration and manufacture of target components, which does not require separation of the alloy components.

A target with an area ratio S(Ag)/S(Pd) = 20.8/79.2 was used to obtain a film with a silver content of 23%, which is optimal in terms of hydrogen permeability and mechanical properties [1]. As a result of sputtering for 40 minutes, a sample with a thickness of 1.1 microns was obtained, and the chemical composition of the silver content in the sample was 23.2 ± 0.7%.

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