

Study of Hydrogen Accumulation in Palladium and Silver-Palladium Alloy

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Abstract. This work presents the results of investigation of the hydrogen accumulation characteristics in palladium, silver and palladium-silver alloy ($\text{Pd}_{60}\text{Ag}_{40}$) at their saturation with hydrogen from different aggregate states of the ambient medium (plasma, liquid, hydrogen atmosphere). The presence of silver in the alloy of palladium-silver leads to the following features: the capture of hydrogen by Pd and $\text{Pd}_{60}\text{Ag}_{40}$ samples depends on the method of saturation. In the case, while plasma and electrolytic hydrogen saturation in both samples is being trapped in the same type of traps (not significantly different in binding energy). While the saturation by Sieverts method takes place, traps formed are characteristic for each type of the samples. In case of electrolytic and plasma saturation in palladium and palladium-silver alloy, the main type of trap is the binding of hydrogen in palladium hydride. Alloying palladium with silver does not lead to decreasing the sorption capacity of the alloy $\text{Pd}_{60}\text{Ag}_{40}$ compared to Pd.

1. Introduction

It is known that palladium is widely used for solving a wide range of problems in hydrogen energetics. However there is a deficiency of palladium which seriously impedes its use, particularly, for the membrane manufacture (e.g., in membrane reactors for the production of ultra-pure hydrogen [1-5]). The deficiency is that the alternate heating and cooling of palladium in a hydrogen atmosphere makes it gradually brittle and deformed. At the same time, some of palladium-silver alloys are able to work in an atmosphere of hydrogen without losing their mechanical strength for a long time [4].

The results presented below are development of the research [6].

The aim of this article is to clarify the influence of silver on the capture of hydrogen by palladium-silver alloy. First of all, it is necessary to examine the efficiency of hydrogen capture into palladium, silver and palladium-silver alloy (in this case a $\text{Pd}_{60}\text{Ag}_{40}$ alloy) by the different saturation methods:

- 1) From the plasma of high-frequency discharge (HFD),
- 2) From electrolyte (in an electrolytic cell at using of studied samples as cathodes),
- 3) From the gas phase at elevated temperature and pressure (Sieverts method).

The samples were investigated by thermally out gassing (TOG) (which is the same thermally stimulated desorption (TSD)) and X-ray phase analysis (XPA) methods.

2. Materials and experimental methods

Samples of palladium and palladium-silver alloy ($\text{Pd}_{60}\text{Ag}_{40}$) were made of sheet material in the form of rectangular plates $25 \times 5 \times 0.1 \text{ mm}^3$, and silver samples in the form of rectangular plates $25 \times 5 \times 2 \text{ mm}^3$



(jeweler argentums). Each sample was saturated repeatedly both in the delivery condition and after "saturation-TOG" cycles. The obtained TOG temperature spectra were normalized to the sample volume.

To study the hydrogen accumulation during the electrolytic saturation of palladium samples, silver, and Pd₆₀Ag₄₀ alloy samples, 1M H₂SO₄ electrolyte on the basis of distilled water was used. Saturation was carried out for t=6 min (for Pd and Pd₆₀Ag₄₀ samples) and from 6 to 80 min (for Ag samples) at a current density J=0.24 A/cm².

Parameters of saturation regime by Sieverts method are: sample temperature T=100°C, pressure P=2 atm., saturation time t=2 hours.

Parameters of plasma saturation regime are: sample temperature T=150°C, the pressure in the saturation chamber P=3·10⁻¹ Torr, the saturation time t=80 min.

The specified parameters of saturation are chosen so that intensity of the hydrogen yield at TOG was observed in one order of magnitude for all samples.

The installation for studying thermal- and radiation- stimulated outgassing of General Physics department of Tomsk Polytechnic University (TPU) and the international scientifically-educational laboratory "Technologies of hydrogen power engineering" TPU was used. It was also used to study the evolution of hydrogen thermally stimulated from the samples. During the study we carried out the analysis of dependences of the hydrogen yield intensities on temperature (the temperature spectra) of thermally outgassing. Linear heating of samples has carried out in the temperature range from room temperature to 1000°C.

Investigations of phase composition of the samples were carried out at the station "Anomalous Scattering" (channel number 2), Siberian Center for Synchrotron and Terahertz radiation, Novosibirsk. The parameters used in the system are: X-ray energy range: 5–20 keV; the size of the input beam: 5×(0.1–1.5) mm²; the time to set diffractograms – from 0.2; resolution of the diffractometer: $\Delta d/d \sim 10^{-4}$ in a high-resolution mode and $\Delta d/d \sim 10^{-3}$ – in the mode of one-coordinate detector.

The binding energies of hydrogen atoms in traps (E_b) shown in figures were estimated according to standard curves given in [6].

3. Results and discussion

Fig. 1 presents the TOG H₂ spectra from Pd and Pd₆₀Ag₄₀ alloy samples saturated by electrolytic method. The figure 1 shows that the spectra are of about the same maximum intensity and the peaks are located at the same temperature ~ 360°C (which corresponds to the binding energy of hydrogen in traps E_b ~ 1.9 eV). In addition, the palladium-silver alloy is observed to have a feature at ~ 410°C (E_b~2 eV). The intensity of the peaks of TOG H₂ spectra of palladium and palladium-silver alloy is almost identical, and the values of the integrals under the curves are (shown in Fig. 4–5): $I_{\text{Pd60Ag40}}/I_{\text{Pd}} \approx 6848/4994 \approx 1.37$.

Fig. 2 shows the TOG H₂ spectra from the Pd and alloy Pd₆₀Ag₄₀ samples saturated from the gas phase (Sieverts method). As it can be seen in the figure 2, after the saturation from the gas phase in the palladium and palladium-silver samples the binding energy of hydrogen in the traps is, as well as in the previous case, 2eV and 1.8 eV respectively. The spectrum of the hydrogen outgassing from the palladium-silver sample is shifted to the area of lower temperature by 71°C. In addition, the hydrogen spectrum of the outgassing from the palladium sample shows an unresolved peak (shelf) at 455°C, this temperature corresponds to the binding energy of 2.1 eV. It is also worth to note that the intensity at the peak of the TOG H₂ spectrum of palladium is lower than one of the palladium-silver alloy, and $I_{\text{Pd60Ag40}}/I_{\text{Pd}} \approx 2.4$.

Fig. 3 shows the H₂ TOG spectra from Pd and Pd₆₀Ag₄₀ alloy samples, saturated from the plasma.

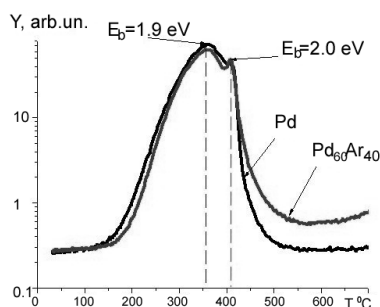


Figure 1. TOG H₂ temperature spectra from samples saturated from the electrolyte

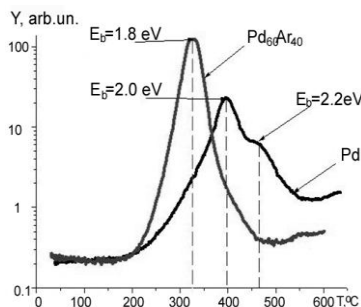


Figure 2. TOG H₂ temperature spectra of samples saturated by Sieverts method

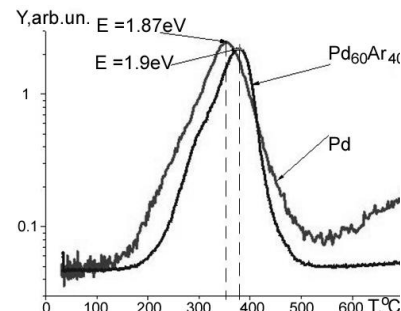


Figure 3. TOG H₂ temperature spectra from samples saturated from the plasma.

As it can be seen from the figure 3, while palladium and palladium-silver samples interact with plasma, hydrogen traps are formed with a binding energy of hydrogen 2eV and 1.8eV respectively. The peak intensity of the spectra from both types of samples is almost the same, and $I_{Pd60Ag40}/I_{Pd} \approx 2,9$. Concerning the temperature (T_m) at which there is a maximum of TOG H₂ spectra, we note the following: T_m of the electrolytic saturation is the same for both materials: $T_m(Pd) = T_m(Pd_{60}Ag_{40})$; while for saturation by Sieverts method $T_m(Pd) > T_m(Pd_{60}Ag_{40})$; with saturation of the plasma $T_m(Pd) < T_m(Pd_{60}Ag_{40})$.

Fig. 4–5 show TOG H₂ spectra of the Pd and Pd₆₀Ag₄₀ samples saturated by three methods: electrolytic, plasma and Sieverts.

It is seen that for Pd samples T_m in the temperature range of ways of saturation "electrolytic (el)–

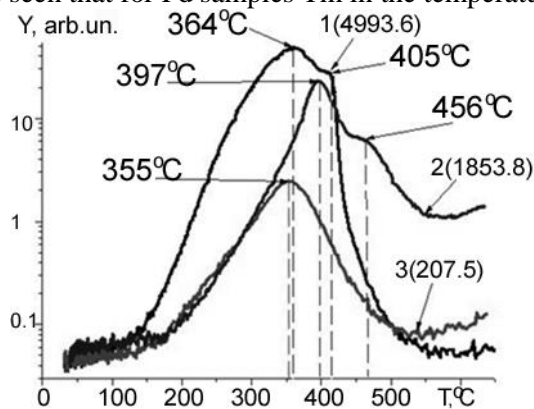


Figure 4. TOG H₂ temperature spectra from Pd samples, saturated by methods: 1 – electrolytic; 2 – Sieverts; 3 – plasma. Numbers in brackets are quantities of integrals (square under curves in standard units).

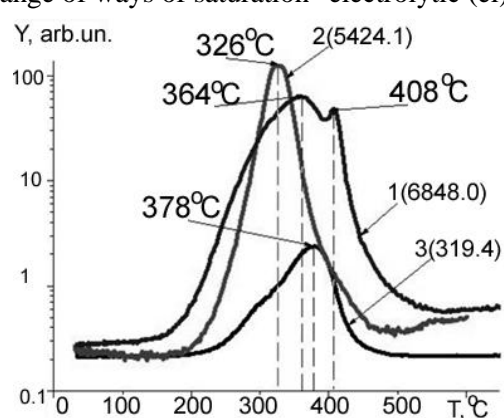


Figure 5. TOG H₂ temperature spectra from Pd₆₀Ag₄₀ samples, saturated by methods: 1 – electrolytic; 2 – Sieverts; 3 – plasma. Inscriptions at the curves is the same as in Fig. 4

Plasma (pl) – Sieverts (Siv)" are in ratio as $T_m(el) \approx T_m(pl) > T_m(Siv)$, and for Pd₆₀Ag₄₀ samples as $T_m(el) \approx T_m(pl) < T_m(Siv)$. Thus, it can be inferred that the type of defects which capture hydrogen during plasma and electrolytic saturation prove to be the same in Pd₆₀Ag₄₀ and Pd. At the same time, the shift of $T_m(Si)$ between the spectra of Pd and Pd₆₀Ag₄₀ reaches 71°C, which indicates that different types of traps are present in these samples at saturation by Sieverts method. The minimum amount of hydrogen is trapped in the plasma saturation, the maximum - in the process of electrolytic saturation. Fig. 6 presents the results of X-ray-phase analysis of Pd and Pd₆₀Ag₄₀ samples before and after hydrogen saturation.

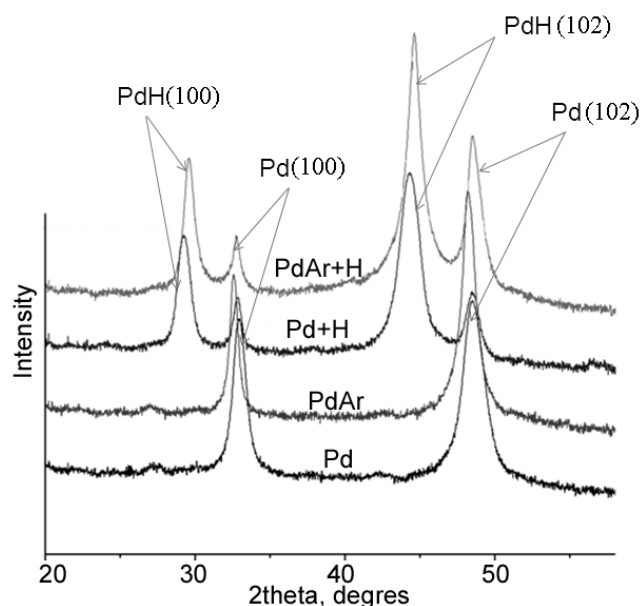


Figure 6. The X-ray diffraction spectra of Pd and Pd₆₀Ag₄₀ before and after hydrogen saturation by electrolytic method. The straight areas in spectra, respectively: Pd, PdAg – before saturation, Pd-H, PdAg-H – after saturation. Arrows specify peaks in spectra, corresponding to separate phases Pd and PdH. Energy of the probing X-ray: 10 keV.

Pd and PdAg curves show the phase compositions of samples before the saturation; Pd-H, PdAg-H – the same samples after hydrogen saturation. Two peaks in each spectrum correspond to the metallic phase of palladium. The presence of silver apparently corresponds to a small shift in the position of the Pd peaks relatively to their position in Pd₆₀Ag₄₀ spectrum (silver displaces palladium atoms in the lattice and not significantly alters the interatomic distance). In the spectra of the saturated samples there is an additional peak (to the left of the peak corresponding to the metallic phase), which corresponds to a Pd-H phase. Note, that there are no peaks observed corresponding to Pd-Ag and Ag-H phases in the X-ray diffraction patterns (Fig. 6), thus, there are no the chemical bonds of silver with palladium or hydrogen in these samples. In other words, no silver hydrides are formed (for their formation high temperatures or (and) pressure are required). This result, first, suggests that the Pd₆₀Ag₄₀ alloy is a solid solution, and the introduced hydrogen (during the electrolytic saturation) bonds only with palladium.

4. Conclusions

1. The capture of hydrogen by Pd and Pd₆₀Ag₄₀ samples depends on the method of saturation. In that case when hydrogen saturation from electrolytic and plasma in both samples is being trapped in the same type of traps (not significantly different in binding energy). While the saturation by Sieverts method takes place, traps formed are characteristic for each type of the samples.
2. In electrolytic and plasma saturation in palladium and palladium-silver alloy the main type of traps is the binding of hydrogen in palladium hydride.
3. Alloying palladium with silver does not lead to a deterioration of sorption capacity of the alloy Pd₆₀Ag₄₀ compared to Pd.
4. The silver in the Pd₆₀Ag₄₀ alloy is in a solid-solution condition.

References

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