Hydrogen electrosorption into Pd-rich Pd–Ru alloys

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ABSTRACT

Hydrogen electrosorption into Pd-rich (>90% Pd in the bulk) Pd–Ru alloys obtained by electrodeposition was studied at 298 K in 0.5 M H_2SO_4 solution using cyclic voltammetry and chronoamperometry. Cyclic voltammograms for pure Pd, pure Ru and a Pd–Ru alloy in a wide range of potentials are compared. Pd–Ru electrodeposits with a small Ru content in the bulk (0.5–2%) can absorb more hydrogen than pure Pd, with the maximum hydrogen-to-metal atomic ratio above 0.80 (as compared with 0.74 for Pd). The maximum absorption capacity of Pd–Ru electrodes containing less than 97% Pd gradually decreases and the H/M ratio drops to ca. 0.40 for electrodes with 90% Pd. The potential of absorbed hydrogen oxidation peak is shifted negatively with decreasing Pd bulk content. The amounts of electrosorbed hydrogen for α and β phase boundaries, i.e. α_{max} and β_{min} have been determined from the integration of the initial parts of current–time responses in hydrogen absorption and desorption processes. The influence of electrode potential on the amount of electrosorbed hydrogen is presented. On the plot of H/M vs. potential the regions of $\alpha \leftrightarrow \beta$ phase transitions are shifted to lower potentials in comparison with pure Pd. The thermodynamic stability of β-phase decreases with decreasing Pd content. The hysteresis effect is observed in chronoamperometric absorption and desorption experiment. The values of maximum, normalized time needed for electrode saturation with hydrogen and its removal with the exception of region containing 97.9–99.6% Pd decrease with increasing Ru bulk content. Hydrogen absorption properties of Pd–Ru electrodes may be explained taking into account changes in electronic and geometric factors probably resulting from alloy formation between Pd and Ru.

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1. Introduction

Since 1866, when Graham published his pioneer work devoted to hydrogen dissolution in Pd and Pd–Ag alloys [1], hydrogen absorption in Pd [1–6] and Pd alloys with other noble metals have been widely examined [7–27]. Hydrogen-alloy systems are still of great interest due to the fact that they can be successfully utilized in many applications such as: nickel-hydride batteries, membranes for hydrogen purification, neutron moderators and catalysts in hydrogenation reaction [28].

The Pd–Ru system exhibits limited solubility in the whole range of compositions depending on temperature. Above 673 K Ru dissolves in Pd forming single-phase, homogeneous faced centered cubic (fcc) solid solution (α-phase). The solubility of Ru in Pd increases with temperature and obtains maximum value in peritectic temperature for sample containing ca. 21% Ru. Further temperature increase causes the formation of liquid and solid (ε) phases of Pd dissolved in hexagonal close packed crystallographic lattice of Ru [29]. However, presented information describe the state of

equilibrium, thus it is possible that data obtained through examination of electrodeposited samples would be inconsistent.

The first electrochemical investigation of Pd–Ru electroplates and their electrocatalytic properties was published by Entina et al. [30] . The authors present that Pd–Ru electrodes have high activity for CH_3OH and $HCOO^-$ oxidation. The Pd–Ru alloys have been investigated mostly in the context of electrocatalysis, olefins' dehydrogenation and hydrogenation processes and membranes for hydrogen purification. There are only a few publications devoted to hydrogen absorption in depicted system. Cabrera et al. described the process of absorption from the gas phase and thermal desorption of hydrogen in Pd and Pd-5% Ru alloy. This research group defines influence of hydrogen absorption on crystallographic orientation of Pd and Pd–Ru surfaces. In a result it was found that the Pd–Ru alloy in comparison with pure Pd withstands more hydrogen absorption–desorption cycles, since the mechanical integrity of the foils is affected by the cycling between absorption–desorption and high-low temperature [31]. Krasilnikova et al. studied the kinetics of hydrogen sorption in the gas phase in Pd–Ru 10% alloy using an adsorption deformation method. The research group stated that alloy contracts on the sorption of hydrogen and the contraction decreases with the temperature. Furthermore, the way of diffusion coefficient determination in alloys was proposed [32].

The Pd–Ru system appears to be interesting in the aspect of hydrogen absorption due to the fact that alloys containing small amounts of Ru are able to absorb more hydrogen than pure Pd [8,33,34]. Wicke and Frölich showed hydrogen absorption isotherms for Pd–Ru with 4% and 10% Ru. For these Ru concentrations the maximum amount of absorbed hydrogen was lower than in Pd with the equilibrium hydrogen pressure shifted towards lower values. However, in the case of Pd–Ru alloy with 1% of Ru the value of the hydrogen-to-metal ratio (H/M) as high as 0.80 was reported [33,34]. The latter feature has been widely investigated in our previous paper [35]. Presented information reveals that the Pd–Ru system requires more investigation in relation to the process of hydrogen electrosorption.

In this paper we report on hydrogen electrosorption in Pd-rich Pd–Ru alloys prepared as thin deposits on Au substrate. We show the influence of electrode potential and alloy bulk composition on the amount of hydrogen absorbed in Pd–Ru electrodes and the presence of various forms of electrosorbed hydrogen. We demonstrate the dependence of the potentials of phase transitions and the extent of absorption/desorption hysteresis on alloy composition. We present the effect of Ru alloying with Pd on the kinetics of hydrogen electrosorption in Pd–Ru electrodes. To the best of our knowledge such a detailed study on hydrogen electrosorption into Pd–Ru alloys has not been performed yet.

2. Experimental

2.1. Materials and equipment

All experiments were carried out in 0.5 M H_2SO_4 solution, deoxygenated with an Ar stream. The solutions were prepared from analytical grade reagents (POCh, Poland) and water triply distilled and purified in a Millipore system. The 298 K temperature was controlled by thermostat Lauda RE 306. The $Hg|Hg_2SO_4|$ 0.5 M H_2SO_4 was used as a reference electrode and Pt gauze as the auxiliary electrode. All potentials are recalculated with respect to the reversible hydrogen electrode in the working solution (RHE). Electrochemical measurements were carried out using a CH Instrument potentiostat (model 604). The working electrode was a gold wire (99.9%, 0.5 mm diameter) covered with a thin Pd–Ru alloy layer (0.7–1.1 μm)

2.2. Preparation of Pd–Ru alloy electrodes

Electrodes were electrodeposited from a bath containing a mixture of 0.11 $PdCl_2$ in 1 M HCl and 0.32 M $RuCl_3$ water solutions. Applied deposition potentials were higher than the value needed for hydrogen absorption to avoid the latter process during alloy formation.

One way to control Pd content in the deposited alloy is modification of the bath composition. In the case of presented samples Ru concentration in baths ranged from 0.27 M to 0.08 M and Pd concentration ranged from 0.0035 M to 0.08 M. Another way to obtain alloys of various compositions is the alteration of the deposition potential maintaining a constant bath composition. In the case of presented samples deposition potentials amounted to: 0.37 V, 0.39 V, 0.41 V and 0.43 V vs. SHE. In this potential range hydrogen sorption does not occur and deposition conditions are far from those corresponding to the phase transition region, where changes in lattice dimensions could modify significantly deposit properties. With decreasing potential the amount of Ru in the alloys increases. This behavior is connected with the fact that due to the difference in standard potentials Pd deposition starts at a higher potential than Ru deposition. Thus, a negative shift of the deposition potential results in a higher ratio of Ru to Pd in the alloy. Using described

methods of varying the deposition conditions (i.e. bath composition and deposition potential) it was possible to obtain Pd–Ru alloys containing 100–90% Pd.

The deposition efficiency ranged from 70% for Pd-rich electrodes to below 10% for electrodes with ca. 90% in the bulk. Therefore, in order to obtain 1 μm electrode thickness the time of deposition was from 300 s for Pd-rich electrodes, to ca. 3600 s for 90% Pd electrode.

Thin alloy layer deposited from chloride solutions was a few times cleaned from chloride ions with strong stream of distilled water. In addition, to avoid impurities, every electrode was kept closed in a glass flask. The lack of chloride ions on the electrode surface was confirmed in CV experiments, where surface electrochemical properties of fresh deposits were identical with those for deposits obtained from other plating solutions (e.g. sulphate bath [36] or for Pd layers prepared by vacuum deposition [37]) as well as Pd samples made of wires or foils [38].

2.3. Characterization of deposits – morphology and roughness factor

Method of electrochemical deposition enables to obtain tight deposits fully covering the gold substrate. Referring to surface morphology in case of Pd and Pd-rich alloys characteristic laminar features 200–800 nm long are visible on the surface. For alloys with higher Ru content the deposit is compact, featureless with bladdery shapes appearing occasionally. Layers deposited from chloride solutions are mostly very rough. The roughness factor was calculated by division of real surface area and geometric surface area of samples. In our experiment real surface area was determined from the charge (voltammetric method) resulting from reduction of surface oxide [39,40]. It was assumed that the electrochemical properties of surface oxides on Pd-rich Pd–Ru alloys are similar to those on pure Pd. This assumption is justified, since alloy surface is homogeneous and Ru content is small, without any separate phases rich in Ru. Such a situation was observed earlier for Pd-rich alloys with Rh or Pt [39].

2.4. Electrode pretreatment procedure

Freshly deposited electrodes were cycled in the hydrogen-oxide region in order to obtain voltammetric characteristic of sample in wide range of potentials. There were only few cycles in the potential range −0.11 V/1.5 V with the scan rate of 0.1 V s^{-1} to avoid Pd dissolution. After described pretreatment electrodes were cycled only in hydrogen region (0.3 V/−0.11 V), where no metals dissolution occurs, until a steady state voltammogram was obtained. This procedure was carried out to avoid effects of aging during further hydrogen insertion/removal. In the case of electrode without hydrogen pretreatment procedure more defects in the crystal lattice can be still created during hydrogen absorption experiment [6], which can cause unrepeatable results. To avoid described so-called effect of aging every electrode was subjected to about 50 cycles of hydrogen insertion and removal.

2.5. The method of composition determination

All alloy compositions given in this work are bulk compositions expressed in atomic percentages. Alloy bulk compositions were obtained by Atomic Emission Spectrometry method (Analytical Laboratory of Polish Mint). Accuracy of atomic emission spectrometry ranges from 90% to 95% of measured value for Pd and from 60% (less than 5×10^{-9} mol Ru) to 90% for Ru. Accuracy depends on the composition of alloys – for samples containing small amounts of elements the accuracy is lower.