Influence of temperature on hydrogen electrosorption into palladium–rhodium alloys



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Introduction

Nearly 150 years ago Graham observed that palladium is able to absorb large amounts of hydrogen. It was a great discovery that put hydrogen amongst other very attractive types of fuel (highenergy, easily-available, non-toxic) has a real possibility to be used on a large scale. The danger of explosion connected with hydrogen storage in gas or liquid phase was the main barrier against its wide



0,02 0,04 0,06 0,08 0,1 E [V] vs RHE

Fig.1 The absorption/ desorption hysteresis for a Pd electrode before and after pretreatment.

usage. Thus, hydrogen storage in the form of metal hydrides seems to be much more safe, economic and convenient. Unfortunately, palladium-hydrogen system is imperfect. Due to its high cost, great atomic mass and significant hysteresis effect (the difference between hydrogen pressure for $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transitions) palladium cannot be used in a practical way. Nevertheless it is a model system widely studied to understand the process of hydrogen absorption in solid materials. And that is why metalhydrogen systems have been still investigated.

Fig.2 The absorption/ desorption hysteresis for a Pd-Rh alloy (91%at.Pd) for two different direction of applied potential.



Fig.3 The absorbtion/ desorption hysteresis for a Pd-Rh alloy (92%at.Pd).

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Experimental

Hydrogen electrosorption into Pd-rich Pd-Rh alloys was studied in acidic solutions (0.5 M H_2SO_4) using cyclic voltammetry and chronoamperometry. All experiments were performed in a threeelectrode cell with a Hg|Hg₂SO₄|0.5 M H₂SO₄ as the reference electrode and a Pt as the auxiliary electrode. The working electrode was a gold wire covered with a thin alloy layer electrodeposited at a constant potential from a bath containing PdCl₂, RhCl₃ and HCl. Various alloy compositions were obtained by changing deposition potential. Hydrogen absorption was performed at a constant potential for a period sufficient to ensure full hydrogen saturation, determined by chronoamperometry. The amount of absorbed hydrogen was calculated from hydrogen sorption and oxidation charges obtained by the integration of chronoamperometric or cyclic voltammetric curves recorded during hydrogen absorption or desorption. Pd content in alloy was computed from the dependence obtained by Żurawski. [1]



Fig.4 The absorption/ desorption hysteresis for different Pd-Rh alloys in 25°C.



Fig.5 The amount of absorbed hydrogen into Pd-Rh alloys in different temperature.

Results and discussion

Preliminary studies have shown that in order to minimize the effect of electrode ageing during the repetitive hydrogen insertion/removal in the experiment proper, freshly deposited alloys have to be subjected to a series of hydrogen absorption/desorption runs until a steady state voltammogram is obtained (Fig.1). It has been found that the direction of applied potential changes during electrode saturation with hydrogen does not influence the electrosorption behavior (Fig.2).

With increasing temperature and Rh content in the alloy bulk the potentials of $\alpha \rightarrow \beta$ and $\beta \rightarrow a$ phase transitions decrease (Fig.3, Fig.4). The potential shift (in comparison to pure Pd) corresponding to the phase transition is explained by the geometric effect, i.e. changes dimensions of the unit cell after creating alloy. In the case of Pd-Rh alloys and other Pd alloys with a lattice constant lower than pure Pd (contracted system) there is a need for an additional work connected with increase size of the crystal lattice during hydrogen absorption in β phase, which is observed in potential decrease for phase transition.



Fig.6 Cyclic voltammetric curves for a Pd-Rh alloy (92%at.Pd) in different temperature.





10°C

Fig.7 The potential of absorbed hydrogen oxidation for different Pd-Rh alloys and different temperature.

With increasing temperature and Rh content in the alloy bulk the hysteresis width decreases (Fig.3, Fig.4) and the potential of absorbed hydrogen oxidation is shifted negatively (Fig.6, Fig.7). The amount of absorbed hydrogen diminishes with increasing temperature (Fig.5). It is also confirmed that for Pd-rich Pd-Rh alloys the amount of absorbed hydrogen is larger than in case of pure Pd (Fig.5) whereas the general rule is that Pd alloys with a non-absorbing metal are characterised by a decrease in the amount of absorbed hydrogen. This decrease is explained by the electronic effect, which consists in filling gaps in the Pd d-band by the other metal electrons. In case of lower Rh content there is increase of number of gaps in the Pd d-band, which is manifested by an increase in the maximum amount of hydrogen absorbed.

The above research is still in progress.

[1] A. Żurawski, Master's Thesis: Badanie elektrosorpcji wodoru w stopach palladowo-rodowych, Warsaw (2005)