

FORMATION OF HYDRIDES IN Pd-Ni ALLOYS

Debowska L., Baranowski B.*

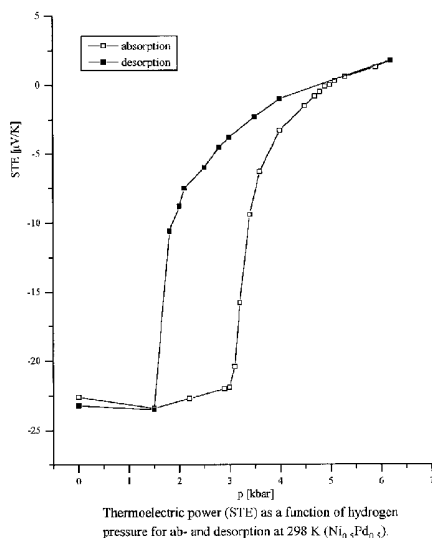
Institute of Physical Chemistry, Polish Academy of Sciences, M.Kasprzaka 44/52
01-224 Warsaw, Poland.

INTRODUCTION

The formation and decomposition pressures of hydrides have been determined in gaseous hydrogen for $\text{Ni}_{0,9}\text{Pd}_{0,1}$, $\text{Ni}_{0,7}\text{Pd}_{0,3}$, $\text{Ni}_{0,5}\text{Pd}_{0,5}$ and $\text{Ni}_{0,3}\text{Pd}_{0,7}$ alloys at 298 K. From the desorption pressures the free energies of hydride formation have been calculated. The results have been compared with values for an ideal system.

EXPERIMENTAL

High hydrogen pressure was created in a piston-cylinder system, where the probes in form of wires about 1 cm long and diameters between 80-250 μm were placed. A special thermostatic system kept the temperature constant. The formation and decomposition pressures have been fixed by thermoelectric power and electrical resistance measurements, whereby phase transitions are accompanied by discontinuous changes of these quantities. The pressures were measured by manganin and Au-Cr gages with an error not exceeding 100 atm. Four probe technique was applied for electrical resistance measurements.



RESULTS AND DISCUSSION

In the figure below an example of thermoelectric power changes measured for the alloy

containing 50 at. % of nickel is presented. All of the values presented were established under stationary conditions.

Following procedure described in [1], the free energies of hydride formation have been calculated basing on desorption pressures.

Palladium and nickel, placed in the same subgroup of the periodic table of elements exhibit a large difference in respect to hydride formation pressure. In palladium the nonstoichiometric hydride forms already at 10^{-2} atm., whereby nearly stoichiometric nickel hydride forms at five orders of magnitude higher pressure. In terms of hydrogen fugacities this difference is higher by two orders of magnitude. In consequence in Pd-Ni alloys a large influence of nickel in the formation pressures is noticed. The free energies of hydride formation calculated earlier for pure elements are -2,8 kcal/mol H_2 for Pd and 5,6 kcal/mol H_2 for Ni. The free energy rapidly increases when nickel is added to palladium.

From free energies of formation for pure elements and the values for alloys the excess was calculated as the difference between the values received and the line connecting palladium with nickel, representing the ideal behaviour.

The excess is positive over the whole composition range and exhibits a maximum about 3,5 kcal/mol H_2 . The maximum appears about 43% Ni in Pd.

CONCLUSIONS

The addition of nickel to palladium considerably increases the formation pressure and - as a consequence - the free energy of formation values. The maximum excess of this quantity appears near the $\text{Ni}_{0,5}\text{Pd}_{0,5}$ alloy.

REFERENCES

1. Baranowski B., Bochenska K. Zeitschrift für Physikalische Chemie Neue Folge 1965; (45):140-152.

* Fax: 48 (022) 632 5276 E-mail: SMF@ichf.edu.pl