Absorption of Hydrogen by Palladium Alloys

PAPERS AT THE WARSAW SYMPOSIUM

Interest in the absorption of hydrogen by palladium and its alloys continues at a high level. A symposium on this subject was held in Poland in July and is reported here, while a further meeting on the subject is planned there for next year. Papers included studies on the diffusion coefficient of hydrogen in gold-palladium alloys, the variation of electrical resistance with hydrogen content of palladium at low temperatures, and the absorption by palladium alloys of hydrogen at extremely high pressures. The symposium also dealt with hydrogen absorption by nickel alloys. Some of these papers parallel work on palladium and are also briefly reported here.

A symposium concerning the absorption of hydrogen by palladium and palladium alloys, and by nickel and nickel alloys, was organised in July by Professor B. Baranowski at the Institute of Physical Chemistry of the Polish Academy of Sciences in Warsaw.

In a general introductory review of transition metal-hydrogen systems, Dr F. A. Lewis of Queen's University Belfast discussed the possibilities of overall correlations between the various groups of solid hydrides of the periodic classification. In particular, attention was drawn to similarities between certain features of the palladium-hydrogen system and hydrides of transition metals of sub-groups 3, 4 and 5, such as non-stoichiometry of solid phases and existence of critical phenomena, metallic properties and appearance, and high diffusivity of hydrogen. A brief outline was given of the theoretical and practical reasons for investigations of the palladium alloy-hydrogen systems which have so far been studied, and also to the possibility of advantages to be obtained from extensions in this field of study.

Gold-Palladium Alloys

Professor Ted B. Flanagan of the University of Vermont presented measurements of diffusion coefficient of hydrogen as a function of hydrogen content in a series of gold-palladium alloys containing from 19 to 56 atom per cent gold. Good agreement was found between results obtained by two independent techniques. A marked variation of the Fick diffusion coefficient as a function of hydrogen content was obtained for alloys where the hydrogen content could be varied over a sufficiently wide range for this to be discerned. The value of the diffusion coefficient at vanishingly small hydrogen contents was virtually unchanged as a function of alloy composition from pure palladium up to 20 per cent gold, and then declined rapidly as a function of the percentage of gold in the alloys.

Low Temperature Studies

Dr T. Skoskiewicz of the Polish Academy of Sciences, Warsaw discussed the changes with variation of hydrogen content of the anomalous variation of the electrical resistance of hydrided palladium with temperature in the vicinity of the related specific heat anomaly occurring at around 60 K. It was advanced that the behaviour could be accounted for in terms of transitions between two forms of palladium hydride possessing

the same Debye temperature and exhibiting virtually parallel relationships between electrical resistance and temperature. A comparison was made of the heat of transformation obtained by integration of the specific heat data and the heat of transformation calculated from the temperature dependence of the concentration of the low temperature modification—as estimated from the measured electrical resistance by considerations of the Nordheim rule. It was concluded that the low temperature form consists of entities of four hydrogens.

High Pressure Studies

Recent extensive study by Professor Baranowski's group in Warsaw of the absorption of hydrogen by palladium and its alloys under high pressures of the gas was reflected in lectures by Professor B. Baranowski and A. W. Szafranski of the Polish Academy of Sciences. Information concerning the techniques employed in measurements of changes of electrical resistance at pressures of hydrogen up to 25,000 atmospheres was presented in both lectures. Professor Baranowski specifically dealt with the palladium-platinum-hydrogen system at 25°C and presented results showing that a maximum in the relationship between electrical resistance and hydrogen content known for the palladium-hydrogen system continued to be present in analogous relationships for palladium-platinum alloys containing up to at least 40 per cent platinum. Generally also it was either shown or indicated that the resistance afterwards decreased to a value close to that of the hydrogen-free metal. Evidence also suggested that for alloys containing >70 per cent platinum the solubility of hydrogen seemed likely to have decreased to very low values.

Szafranski's studies indicated the possibility of substantial further extension of the complex variety of forms of the relationship between electrical resistance and hydrogen content for the silver-palladium series of alloys. Measured changes of electrical resistance suggested that silver alloys containing up to 70 per cent silver were still capable of absorbing significant contents of hydrogen at the highest pressures employed. Certain features of the results indicated some possibility of using the changes of electrical resistance for estimating hydrogen contents and fugacities in the higher ranges of pressure.

Nickel Alloys

Dr H. J. Bauer of the University of Munich reported on the effects of absorption of hydrogen on the electrical and magnetic properties of nickel and nickel-copper alloys. Quantitative differences in the changes of magnetisation due to hydrogen and deuterium during absorption of the respective isotopes indicated that deuterium had a higher mobility than hydrogen in the nickel-copper alloys—in general parallel with comparisons of the diffusibility of hydrogen and deuterium in palladium and palladium alloys. Problems of making measurements of magnetic susceptibility and electrical resistance of nickel hydrides at temperatures below 20 K were discussed, and evidence was presented that some behaviour patterns of these parameters at low temperatures had their origins in the Kondo effect arising from the presence of transition metal impurities in the nickel matrix.

Dr G. Wolf of the Bergakademie, Freiberg, East Germany, presented results of specific heat measurements on samples of nickel hydride over the temperature range 10 to 200 K.

A. Stroka of the Polish Academy of Sciences, Warsaw presented a survey of differences of the thermodynamic parameters relating to the absorption and desorption of hydrogen and deuterium to and from nickel hydrides and deuterides as derived from measurements obtained by high pressure techniques.

It is hoped that a more extended conference concerning this general field of study will take place at Wroclaw, Poland in 1971.

F. A. L.