PRESSURE SYNTHESIS OF TITANIUM AND ZIRCONIUM HYDRIDES

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Titanium and zirconium hydrides of the hydrogen content corresponding to stoichiometric composition MH_2 have been prepared by combining both metals with hydrogen under pressures and temperatures of 20—100 atm and 230—500°C, respectively. A characteristic rapid exothermic course of the reaction has been found and ignition temperature established.

The methods of preparing titanium and zirconium hydrides, described hitherto, consist of two basic techniques. A less common technique makes use of titanium and zirconium dioxides as raw material, which are reduced by calcium[1-5] or magnesium[6-7] hydrides under hydrogenation of the transition metal thus produced. A common technique is hydrogenation of metal in the form of powder, sponge, sheet, or wire. The latter method involves heating of the metal to a high temperature (600—800°C) under vacuum and subsequent admission of hydrogen under normal or reduced pressure in the time, when the apparatus is cooled down[8]. The hydrogenation is carried out also under reduced[9] or normal[10] pressures in a tubular furnace at 500°C. The kinetics of the reaction between metal and hydrogen is little described in the literature. From the point of view of kinetics, only dissolution of hydrogen in metal up to the amount of several atomic percent under reduced pressures to about 0·1 atm[11] has been paid more attention. At the same time, effects of pressure and temperature on the rate of dissolution are rather varying and hardly to be reproduced. Contrary to this, effect of purity of the starting metallic material on final content of hydrogen in hydride is discussed in the literature[12,13].

In this paper, synthesis of titanium and zirconium hydrides carried out under hydrogen pressures from 70—100 atm (starting pressure) to 25—50 atm (final pressure) has been described.

EXPERIMENTAL

Reagents and Apparatus

Titanium sponge (Research Institute of Metals) 99·6% Ti, 0·05% O, 0·008% N, 0·014% C. Zirconium sponge (Institute of Nuclear Research, Czech. Acad. Sci.) 99·8% Zr, 0·056% O, 0·003% N, 0·004% Fe. Electrolytic hydrogen (VCHZ Semtín) 99·9% H, repurified by heating with TiH_2 to 400°C at 200—250 atm.

Rotary autoclave of the 2·5 l content for 200 atm/400°C was heated by the city gas flame under rotation of 60 rev./min. The temperature was measured in the middle part of the vessel by means of a thermocouple, pressure was periodically measured by a pressure gauge for 0—250 atm (precision 0·5%) and mathematically converted for the temperature of 20°C using a graph constructed empirically.

Preparation of TiH_2

Steel balls and 200 g of titanium sponge were put into the autoclave. On flushing with argon and purified hydrogen, the autoclave was made up to the pressure of 74 atm and heated at a rate of approx. 8—10°C/min up to 200°C and then at a rate of about 2—3°C/min. On a attaining 320—325°C, violent exothermic reaction took place, the temperature rose up to 450°C for a short time and pressure decreased from 140 atm (306°C) down to 60 atm (384°C) within 2 min. The pressure fall corresponds to a consumption of 4·5 mol of hydrogen, *i.e.* 108% of the theory related to TiH_2. After cooling down, 201·5 g of powder having hydrogen content of 4·01 (combustion analysis) or 4·09% (thermogravimetric analysis) was obtained; theory for TiH_2 is 4·04% H. The product was heated on a thermobalance under a pressure of $1 \cdot 10^{-6}$ Torr and was decomposed from 98·5% within 330—490°C (rate of heating 6°C/min). Specific surface area 1·47 m^2/g density 3·65 g/cm^3.

Preparation of ZrH_2

Similarly as in the preparation of TiH_2, 254 g of zirconium sponge was employed. The exothermic reaction, however, occurred (at 70 atm, 20°C) at 240 °C, the pressure decreased by 28 atm, which corresponds to the consumption of 102·2% hydrogen, calculated for ZrH_2. The autoclave was cooled down similarly as in the preceding experiment. 253 g of the substance of the hydrogen content 2·30 (combustion analysis) or 2·20% (thermogravimetric analysis) was obtained; ZrH_2 theoretically amounts to 2·16% H. Specific surface area 0·82 m^2/g, density 5·86 g/cm^3. The sample released 98·5% of hydrogen, when heated (4°C/min) from 270 to 600°C under a pressure of $1 \cdot 10^{-6}$ Torr.

Analytical

Hydrogen was determined both by combustion of the sample in the apparatus for elementary analysis and by thermal decomposition on thermobalance Mettler. The density was determined in xylene using a pycnometer, specific surface area by the adsorption method according to Nelsen and Eggertsen[14]. X-ray measurements were carried out by means of apparatus Mikrometa 2 (Chirana) using the Debye-Scherrer method. Relative intensities were determined visually.

RESULTS

It was found that the ignition temperature is highly influenced by purity of the hydrogen used. When using hydrogen of purity 99·9%, the ignition temperature is (under comparable conditions) by about 100—110°C higher for titanium than if purified hydrogen is employed. Addition of ready hydride into the reaction vessel (5% of the metal weight) has a similar, but smaller effect. This effect can be explained by the fact that active impurities, such as oxygen and nitrogen, contained in hydrogen, react with the metal surface and the reaction products make the metal surface passive towards hydrogen. On the contrary, the hydride added reacts with these gases preferentially.

Considerable differences were established likewise in the behaviour of zirconium sponge and sheet of equal purity of 99·9%. During hydrogenation of the sheet, several hours heating of the sheet to the temperature of 400–450°C was needed till the characteristic exothermic reaction was attained. The course of hydrogenation, however, was similar to that of the sponge, *i.e.* all of the hydrogen was consumed within a short time during the exothermic reaction.

Whereas the X-ray patterns of the zirconium hydride prepared correspond to those of the reagent measured by Vaughan and Bridge[15], two lines of medium intensity (d 1·71 Å and 1·67 Å and I/I_0 60, or 40) which are not presented in the literature[16,17] were, in addition, found in the TiH_2 sample.

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