Supplementary Information

Thermodynamic characterisation and application of the ZrNi-H metal hydride system in the low-pressure regime

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Experimental details

Test bench specifications & instrumentation

The test bench is a configuration of one Sieverts' volume (V_S), composed of commercial vacuum flange components (316 L stainless steel parts, aluminium-sealed) and separated by different pneumatically controlled valves (PV) to connect the vacuum pump (VP) and hydrogen supply (H_2 5.0) as well as to allow the attachment of the reactor volume (V_R) containing the metal hydride sample.

The instrumentation of the test bench (overview given in Table S1) includes capacitive vacuum pressure gauges to determine the absolute gas pressure and thermocouples of type K to measure the temperature inside of the Sieverts' volume (T_S) and the ambient temperature (T_{amb}). Two pressure sensors (p_{01},p_{02}) of the same type with successive measurement ranges are installed to extend the covered measuring range. During post-processing, these are combined to form one temporal pressure curve p.

Further, type K thermocouples are mounted both inside and on the sample reactor to determine the temperature of the reaction bulk (T_R), the reactor wall ($T_{R,w}$) and the thermal oil (T_{oil}) over time. All applied thermocouples are calibrated. The reasonable range of application of the test infrastructure is 0.01-1000 mbar (pressure) and -20-160 °C (temperature) due to the limitations of the pressure sensors used and the thermal oil in operation at atmosphere.

The size of the Sieverts' and reactor volumes given in Table S2 are determined by the gas expansion method[1]. The listed values are mean values from several different measurement runs, together with the standard deviation[2]. The leakage rate Q_L is calculated from the pressure increase in the entire test volume ($V_S + V_R$) over a duration of 450 h.

Table S1 - Specification of the test infrastructure's measurement quantities.

Quantity	Instrument	Measuring range	Uncertainty
T_S	Thermocouple type K	18 - -28 °C	± 1.0 K (max.)
T_{arb}			
T_R		-5 - 160 °C	
T_{Rv}			
T_d			
p_{01}	Capacitive transmitter (Pfeiffer CMR 361)	0.1-1100 mbar	± 8.0 10^{-4} + 2.1 10^{-3} M.V.
p_{02}	Capacitive transmitter (Pfeiffer CMR 363)	0.001-11 mbar	

Table S2 - Specification of the Sieverts' volume (V_S) of the test bench and the reactor void volume (V_R) as well as the obtained leakage rate in both volumes.

Quantity	Value
V_S	5.798 ± 0.0028 10^{-3} m^3
V_R	0.401 ± 0.007 10^{-3} m^3
$Q_{L\,\mathrm{in}}\ V_S + V_R$	1.69 10^{-7} mbar l/s = 7.69 10^{-8} Pa m^3/s

Test reactor

The reactor is built of 316 L stainless steel vacuum components, partly ISO-KF components and the lower part, which is inside the thermostatic bath, is made of ISO-CF components to protect it from thermal oil and occurring temperature variations, thus ensuring the tightness of the reactor.

The thermocouple for detecting the temperature of the metal hydride bulk inside the reactor is welded into the base plate. The sensor tip is located centrally and at a height of approx. 2 mm. Inside the reactor, a circular sintered metal filter (manufacturer: gkn SIKA, pore size 0.5 µm) is welded into the reactor tube to separate the released hydrogen from the metal hydride powder.

Materials

Metal hydride: ZrNi, 1:1 by atom, purchased from MAHYTEC, manufacturer's declaration of purity: 99.50% (Zr), 99.93% (Ni), grain size < 2 mm, storage mode under argon 4.5). The material is stored permanently in a glove box under pressurized argon atmosphere, where it was also weighed and filled into the shown reactor.

Hydrogen gas: The test setup is located in a lab with central hydrogen 5.0 supply line at a pressure of 300 bar which is stepwisely reduced until the vacuum test bench.

Activation of the metal hydride samples

The void volume of the reactor is determined anew with each sample. The bulk material in the reactor is similarly activated at the test facility prior to the experiments. The sample is heated to about 160 °C and at the same time evacuated for several hours (min. 17 h). Hydrogen is then added up to 1000 mbar and temperature cycles between -10 and 160 °C are run for 2 hours each (30 min for heating and cooling between temperature steps). The activation starts in the first cycles, a total of at least 10 cycles are run until a repeatable reaction behaviour can be observed. Due to the low sample masses, the

supplied hydrogen mass (in terms of applied initial pressure for activation in the given size of the Sieverts' volume) leads to hydrogen loadings clearly beyond the expected plateau range. Therefore, after the first successful activation cycles, the amount of hydrogen in the system is reduced to obtain hydrogen concentration values within the $\beta + \gamma$-plateau.

The first absorption of hydrogen started during the cooling phase after the first half cycle of the activation. In total, 15 cycles are performed, of which the last 7 each show identical behaviour and the sample is thus considered to be fully activated.

Measurement procedure and data evaluation

Between 50 °C and 150 °C, 7 different temperature levels in steps of 25 K are run.

ZrNi sample I**:** In order to give a comprehensive and reliable picture of the sorption behaviour characterisation of ZrNi in the range of 0-150 °C, 26 measurement runs are carried out at 17 different initial loadings between 0.60 and 1.73wt.%.

ZrNi sample II**:** In the temperature range of 25-150 °C, 10 different measurement runs loadings are performed at 7 different initial. Sample II is used in particular to investigate the low hydrogen capacity range of the $\beta + \gamma$ plateau, so the majority of the runs are in the hydrogen concentration range of 0.52-0.94wt.%. For comparison with sample I, a measurement run is conducted in the middle of the plateau (1.28wt.%).

The resulting pressure values for 0 °C and 25 °C have been found to be so low that they could not be recorded with sufficient accuracy using the existing pressure measuring sensors. As a result of the limited credibility and reproducibility, the measured data are only shown between 50 °C and 150 °C.

Equilibration criterion: The averaged values of the last 5 min of each temperature step of the pyramid-shaped driving temperature profile are extracted. The steady-state criterion requires the moving averaged temporal pressure signal (5-minute-window) deviates less than 0.25% within 30 minutes[22].

If it is fulfilled, the reaction is considered as being in equilibrium and the corresponding temperature and pressure values are post-processed for the pressure-composition-temperature curves.

References

1. K. J. Gross, K. R. Carrington, S. Barcelo, A. Karkamkar, J. Purewal, S. Ma, H.-C. Zhou, P. Dantzer, K. Ott, T. Burrell, T. Semeslberger, Y. Pivak, B. Dam and D. Chandra, *Recommended Best Practices for the Characterization of Storage Properties of Hydrogen Storage Materials*, National Renewable Energy Laboratory, USA, 2010.
2. J. Felbinger, I. Bürger and M. Linder, *International Journal of Hydrogen Energy*, 2023, **48**, 36849-36865.