High-pressure and high-temperature x-ray diffraction cell for combined pressure, composition, and temperature measurements of hydrides

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We present the design and construction of a high-pressure (200 bars) and high-temperature (600 °C) x-ray diffraction (XRD) cell for the *in situ* investigation of the hydrogen sorption of hydrides. In combination with a pressure, composition, and temperature system, simultaneous XRD and volumetric measurements become accessible. The cell consists of an x-ray semi-transparent hemispherical beryllium (Be) dome covering a heatable sample stage, which simultaneously allows sample temperatures of up to 600 °C in an applied hydrogen atmosphere of up to 200 bars. The system volume is as low as possible to maximize the precision of the volumetric measurements. Due to the high thermal conductivity of hydrogen, and in order to preserve the mechanical stability of the beryllium, the cell is water cooled. Its operability was studied on the example of the hydrogen absorption of Mg₂Ni. The advantages and limitations of the proposed design are discussed. © 2011 American Institute of Physics. [doi:10.1063/1.3600668]

I. INTRODUCTION

The thermodynamic properties of a hydrogen storage material are crucial, as they determine the operating conditions, i.e., the working temperature and pressure.¹ The high-pressure and -temperature x-ray diffraction cell offers the possibility to simultaneously investigate structural properties such as phase changes during de- and rehydrogenation of hydrides together with thermodynamic properties such as the enthalpy and entropy of reaction. This is realized by the conjunction of an x-ray transparent gas tight sample cell, and a volumetric pressure, composition, Temperature (pcT) system. Additionally the pcT system can be used as a dosing system to control the pressure during experiments, e.g., for isobaric measurements.

A. Thermodynamics of metal hydrides

Metal hydrides are metals or alloys that have the property to dissolve and absorb a large amount of hydrogen, e.g., $\text{Mg}_2\text{Ni} + 2 \text{H}_2 \leftrightarrow \text{Mg}_2\text{NiH}_{0.3}$ (α -phase) + 1.85 $\text{H}_2 \leftrightarrow \text{Mg}_2\text{NiH}_4$ (β -phase).² During hydrogenation of a metal at a constant temperature and low hydrogen concentration, a solid solution of hydrogen in the metal is formed, commonly referred to as the α -phase. At a higher concentration the metal hydride (β -phase) is formed on the expense of the α -phase. During the formation of the β -phase both phases coexist and result in a pressure plateau in the corresponding pcT isotherm. For each temperature there exists an equilibrium pressure p_{eq} .

The thermodynamic parameters (enthalpy ΔH , and entropy ΔS) can be determined by plotting the logarithm of the equilibrium pressure p_{eq} divided by the standard pressure p_0 (1.01325 bars) as a function of the inverse temperature in the so-called Van 't Hoff plot, defined by the following equation:³

$$\ln \left(\frac{p_{\text{eq}}}{p_0} \right) = \frac{\Delta H}{R} \frac{1}{T} - \frac{\Delta S}{R}. \quad (1)$$

The ideal gas constant is $R = 8.31447 \text{ J mol}^{-1} \text{ K}^{-1}$. The slope of the straight line is proportional to ΔH and the y-axis intercept is proportional to ΔS . By setting $p_{\text{eq}} = p_0$, the desorption temperature can be determined by $T_{\text{dec}} = \Delta H / \Delta S$. For our reference system Mg₂NiH₄ (Ref. 2) the following values are given in literature: $\Delta H = -64.5 \text{ kJ mol}^{-1} \text{ H}_2$ and $\Delta S = -122.2 \text{ J K}^{-1} \text{ mol}^{-1} \text{ H}_2$, leading to an equilibrium temperature of $T_{\text{dec}} = 255 \text{ °C}$ at $p_{\text{eq}} = p_0$. In general during hydrogenation the volume expansion of a typical hydride can reach 10–30%.⁴

B. pcT instrument and dynamic measuring method

In the dynamic pcT method, pressure composition isotherms are recorded at different flow rates. The equilibrium state is thereby determined by the extrapolation to zero flow. The logarithms of the measured plateau pressures $\ln(p_{\text{des}}/p_0)$ are linearly extrapolated to zero flow to assess the equilibrium pressures p_{eq} . This type of pcT system and the measuring method are described in detail by Biemann *et al.*⁵ The dynamic pcT method was successfully used to determine the stabilities of LiBH₄,⁶ NaBH₄,⁷ and the LiBH₄/CeH₂ (Ref. 8) composite system.

C. Requirements for a combined measurement

For the combined measurements we require (1) high pressure up to 200 bars, which is the industrial standard for compressed gas, (2) high temperature up to 600 °C to follow, for example, the thermal desorption of borohydrides, (3) big

sample volume, and (4) low cell volume with respect to the amount of gas desorbed to facilitate the pcT measurements.

Conventional powder x-ray diffraction measurements performed with glass capillaries suffer from a limited pressure resistance, especially at higher temperatures. A further disadvantage is the little sample volume that is too small for simultaneous volumetric measurements. The sample volume of the sample holder of the high pressure cell is 0.212 cm^3 , which is almost ten times larger compared to a 0.8 mm diameter glass capillary with a sample volume of only 0.025 cm^3 when filled to a height of 5 cm.

Commercially available x-ray diffraction (XRD) cells are usually designed for vacuum or inert gas atmosphere to protect air-sensitive samples. They are usually not suited for higher gas pressures. Anton-Paar offers the XRK 900 reactor chamber⁹ which reaches a temperature of 900°C and a pressure of 10 bars. The x-ray windows have a design of a cylindrical section and consists of a Kapton housing and a beryllium heat shielding. The TCP 20 from MRI GmbH (Ref. 10) is a chamber that allows a sample temperature of 1000°C in a pressurized atmosphere up to 20 bars. In the literature different XRD cell designs can be found as, e.g., Bernard *et al.*¹¹ who published a design of an ultra high vacuum XRD chamber consisting of a cylindrical beryllium window that can also be pressurized to several bars, in which the sample can be heated up to 927°C . Huo *et al.*¹² constructed a high pressure (70 bars) and low temperature (-196 – 25°C) cell for hydrate studies, consisting of a beryllium cylinder with an inner diameter of 1.5 cm. Nowak *et al.*¹³ describe a ultra high vacuum XRD chamber with a 5 cm diameter beryllium dome in which the sample can be heated up to 900°C . The chamber is designed for the operation at a synchrotron.

We designed and tested a cell to simultaneously fulfil all the requirements for combined XRD and pcT measurements for hydride research. The cell consists of an x-ray semi-transparent hemispherical beryllium dome covering a heatable sample stage, which simultaneously allows sample temperatures of up to 600°C in an applied hydrogen atmosphere of up to 200 bars.

II. INSTRUMENTAL

A. Design of the XRD cell

Beryllium has several physical properties that make it the material of choice for an XRD dome. It is relatively transparent for x-rays with a mass attenuation coefficient of $\mu/\rho = 1.091 \text{ cm}^2 \text{ g}^{-1}$ (Ref. 14) ($\rho = 1.85 \text{ g cm}^{-3}$) at a photon energy of 8.0478 keV ($\text{Cu K}_{\alpha 1}$ radiation) corresponding to a wave length of $1.5406 \text{ \AA}$. It is mechanically strong with a tensile strength of $\sigma(20^\circ\text{C}) = 425 \text{ MPa}$ (Ref. 15) and it has a high thermal conductivity of $\lambda_{\text{th}} = 216 \text{ W m}^{-1} \text{ K}^{-1}$.¹⁵ The major disadvantage of beryllium is its toxicity, especially when inhaled in the form of small particles.¹⁶ The geometrical form of a hemisphere reaches the highest mechanical stability with the least amount of material, in order to have the lowest absorption of x-rays possible. An additional advantage of this geometry is that the path length of the x-rays through the beryllium is independent of the measuring angle and therefore

no angle dependant correction for the absorption is needed. For a wall thickness of $d_w = 0.17 \text{ cm}$ half of the x-ray intensity is absorbed on the way through the Be dome to the sample and back ($2d_w$),¹⁷

$$I/I_0 = \exp(-(\mu/\rho)\rho 2d_w) = 0.5. \quad (2)$$

The mechanical strain σ in a hemispherical sphere with an inner diameter d_i and a wall thickness d_w can be calculated as follows:¹⁸

$$\sigma = (\Delta p d_i) / (4d_w), \quad (3)$$

where Δp is the pressure difference between the inside and outside of the sphere. With the above given value for d_w and $d_i = 1.5 \text{ cm}$ the maximum pressure difference is $\Delta p = 963 \text{ bars}$. If the pressure cell is operated at 200 bars, there is a security factor of around 5 at room temperature. For low temperatures (0 – 200°C) the tensile strength is decreasing linearly as a function of temperature. At 200°C the tensile strength is $\sigma(200^\circ\text{C}) = 380 \text{ MPa}$ (Ref. 15) and the maximal pressure difference would be $\Delta p = 861 \text{ bars}$. For temperatures exceeding 200°C the tensile strength is decreasing more than linearly, therefore the Be dome has to be cooled below 200°C in order to maintain the high security factor.

The Be dome consists of a hemispherical part as described above, a cylindrical part in the middle with twice the thickness as the hemisphere, and a thick cylindrical part where the dome is fixed to a stainless steel flange. The whole dome is machined out of a single piece of beryllium. A cross section of the Be dome and the pressure cell is shown in Fig. 1.

The Be dome and the stainless steel flange were supplied by Brush Wellman.¹⁹ The dome is brazed to a stainless steel flange with cusil, a copper silver alloy as the brazing material. The cooling of the Be dome is accomplished with bores inside the stainless steel flange with welded steel tubes where the water cooling circuit is connected. Due to the good thermal conductivity of beryllium and the fact that the dome is brazed to the water cooled steel flange, the heat on the dome is expected to be well dissipated. The bottom flange is cooled in the same way in order to cool the lower part of the cell. The body of the pressure cell consists of a cylindri-

FIG. 1. Layout of the high-pressure and high-temperature XRD cell.

FIG. 2. Picture of the XRD cell installed in the XRD hutch.

cal tube with a flange at the top and at the bottom. A 2.54 cm diameter ceramic sample heater was supplied by HeatWave Labs, Inc.²⁰ which allows heating the sample up to a temperature of 600 °C at 200 bars of hydrogen. The area around the heater is isolated with Al₂O₃ ceramic, filling almost all the empty space inside the pressure cell in order to have a small internal empty volume. Also the empty space in the heater was filled with an insulating material. The bottom flange has electricity feedthroughs for the heater and a thin flexible (0.01 in.) thermoelement (K-type) that is placed inside the bottom of the sample holder. The top and bottom flange are fixed with screws and sealed with O-rings to the body of the cell. The cell is mounted on an adjustable z-table in order to fine tune the surface of the sample with respect to the beam position. Furthermore, it can be levelled out hori-

zontally to ensure a parallel sample surface. A picture of the cell inside the XRD hutch is shown in Fig. 2.

The aluminium sample holder has a diameter of 2.54 cm and a height of 4 mm. The sample cavity is 1.34 cm in diameter and 1.5 mm deep. Below the sample cavity a hole is drilled into the sample holder, where the thin flexible (0.01 in.) thermoelement (K-type) is placed (Fig. 1). Due to the fact that during the hydrogen sorption the sample may undergo a volume change and could loose the good thermal contact with the sample holder, it was designed with the possibility to slide a thin (100 μm) Be foil over the sample. In this case the absorption will be angle dependant and in Eq. (2) the absorption due to the Be foil with thickness d_f has to be added,

$$I(2\theta)/I_0 = \exp(-(\mu/\rho) \rho_2 (d_w + d_f/\sin(\theta))). \quad (4)$$

B. Simulation of the XRD cell

In order to understand the heat transfer in the whole cell, it was modelled and numerically simulated by finite element method (FEM) analysis (Comsol Multiphysics²¹). For the solid phases heat conduction, surface to surface (inside the cell) and surface to ambient radiation (outside) was applied. For the gas phase, the heat conduction and free convection due to the temperature dependant density/pressure was taken into consideration. Due to the axial symmetry of the cell it was simulated in a two dimensional model (z- and r-axes). The heat conductivity of metal hydride powders is generally very low (1–2 W m⁻¹ K⁻¹),²² gas type and pressure dependant. The heat conductivity as a function of the pressure shows an S-shaped curve. Between 10⁻³ and 1 bars (Knudsen Number: 10 > Kn > 0.01) the heat conductivity increases sharply as a function of the pressure and is almost constant outside this

FIG. 3. Simulation of the temperature distribution in the XRD cell for $P = 90$ W, $p = 20$ bars hydrogen, and a cooling water temperature of $T_c = 15$ °C.

FIG. 4. Simulation of the temperature distribution in the Be dome for $P = 180$ W at $p = 20$ bars hydrogen ($T_s = 555$ °C) and $T_c = 15$ °C ($\Delta T_{\text{isotherm}} = 1$ °C).

pressure range.²³ Because the hydrogen pressure was higher than 1 bar, for simplicity a constant value of the heat conductivity of $1.2 \text{ W m}^{-1} \text{ K}^{-1}$ was assumed for the hydride sample in all simulations.

A section of a simulation of the temperature distribution in the cell at $p = 20$ bars hydrogen and a heating power of $P = 90$ W is shown in Fig. 3. The temperature of the cooling

water was always fixed to $T_c = 15$ °C. The hydrogen convection is clearly seen inside the dome.

As mentioned in Sec. II A due to mechanical stability reasons the temperature of the Be dome should not exceed 200 °C. The temperature distribution in the Be dome at a pressure $p = 20$ bars hydrogen and a heating power $P = 180$ W (corresponding to a sample holder temperature $T_s = 555$ °C)

FIG. 5. Simulation of the temperature distribution in the sample (heat conductivity $\lambda_{\text{th}} = 1.2 \text{ W m}^{-1} \text{ K}^{-1}$) and an aluminium sample holder, $P = 90$ W, $p = 20$ bars hydrogen, and $T_c = 15$ °C ($\Delta T_{\text{isotherm}} = 1$ °C).

is shown in Fig. 4. At the top the temperature is 98 °C and at the connection to the steel frame it decreases to 60 °C, showing that the water cooling is efficient enough.

Ideally the sample temperature should be homogeneous over the entire sample volume. As the sample is heated from the bottom and cooled from the top, we expect a temperature gradient within the sample, especially for samples with very low heat conductivity such as metal hydrides. The temperature distribution in the sample at $p = 20$ bars and $P = 90$ W (corresponding to $T_s = 319$ °C) is shown in Fig. 5. The highest temperature gradient is in the middle of the sample along the z -direction. In this direction the temperature difference is ~ 7 °C and is decreasing radially to ~ 2 °C at the border. Due to the axial symmetry the contribution to the total sample volume is higher at the border than in the middle.

One approach to decrease the temperature gradient would be to reduce the cooling of the cell to the minimum. Another possibility would be to make the sample holder with fins that reach into the sample. The overall sample thickness would then be smaller and consequently also the temperature gradient.

III. INSTRUMENT PERFORMANCE

A. X-ray absorption

In order to measure the absorption of the Be dome, a silicon powder pattern was measured with and without the Be dome. As shown in Fig. 6, the absorption due to the Be dome is 60%, which is in rather good agreement with the calculation (50%).

The empty volume of the cell was determined to be 32 cm³.

B. Thermal behaviour

Experimentally the overall cooling effect of the hydrogen gas was determined by measuring the heating power necessary to reach a certain temperature of the sample holder. Figure 7 shows the heating power as a function of the hydrogen pressure (measured at 0.1, 1, 10, 30, and 100 bars) for different sample holder temperatures (50–600 °C). The variation is highest for small pressures and converges at higher

FIG. 6. XRD of Si powder with and without the Be dome. 60% of the intensity is absorbed by the Be dome.

FIG. 7. Heating power P as a function of the hydrogen pressure p for different sample holder temperatures T_s .

pressure. At a given pressure, the heating power is almost linear as a function of sample holder temperature.

The simulated and measured values for the heating power and sample holder temperature correlate well as shown below. For a simulated heating power of 90 W at $p = 20$ bars (Fig. 5) a sample holder temperature of 320 °C is reached versus 104 W extrapolated from the measured values (Fig. 7) necessary for reaching the same temperature. A simulated heating power of 180 W at $p = 20$ bars leads to $T_s = 555$ °C (conditions as in Fig. 4) versus 200 W extrapolated from the measured values (Fig. 7) for the same conditions.

In Fig. 8 the measured Be dome temperature (top) is shown as a function of the hydrogen pressure for $T_s = 600$ °C. The extrapolated temperature of 155 °C at 200 bars hydrogen is below the upper limit of 200 °C set for security reasons.

The simulation at the parameters $P = 180$ W, $p = 20$ bars, $T_s = 555$ °C predicts a dome temperature of 98 °C which is in good agreement with experimental measurements, yielding 98 °C at $P = 180$ W, $p = 20$ bars, and $T_s = 600$ °C.

C. Measurements of Mg₂NiH₄

The XRD cell is installed in a Bruker D8 Advance diffractometer. The used radiation is Cu-K α ($\lambda = 1.5418$ Å) using a parallel incident beam prepared by a Göbel x-ray mir-

FIG. 8. Be dome (top) temperature as a function of the hydrogen pressure for $T_s = 600$ °C.

FIG. 9. Isotherms (343, 353, and 363 °C) of the hydrogen absorption of Mg_2Ni at a hydrogen flow of 2 SCCM.

ror in combination with a linear detector (VÅNTEC). The pcT system is placed inside the XRD hutch to minimize the system volume of the overall setup. During a pcT measurement the pressure is measured as a function of the amount of hydrogen de- or absorbed from the sample.

Three hydrogen absorption isotherms of 213 mg Mg_2Ni measured at 343, 353, and 363 °C at a hydrogen flow of $f = 2$ SCCM (SCCM denotes cubic centimeters per minute at standard temperature and pressure) are shown in Fig. 9. Two plateaus can be identified, the lower one corresponds to the formation of MgH_2 due to some excess Mg and the second corresponds to the formation of Mg_2NiH_4 . For each isotherm, the plateau pressure of desorption $\ln(p_{\text{eq}})$ was taken at the maximum of $dc/d(\ln(p))$,⁵ where c [mass %] is the hydrogen amount desorbed by the sample (Fig. 10, isotherm at 353 °C). Two isotherms (343 °C) measured at two different flows (1 and 2 SCCM) are shown in Fig. 11. The isotherms are very similar and the equilibrium pressures are almost the same (inset, Fig. 11), indicating that the kinetics of the material is very fast. It can be expected that at higher temperatures the kinetics is at least as fast as for 343 °C, therefore only one flow (2 SCCM) was measured without extrapolation to zero flow. All equilibrium pressures are plotted in Fig. 12 as a function of the inverse temperature. By applying the Van 't Hoff equation (1)

FIG. 10. The hydrogen amount c is plotted as a function of $\ln(p)$. Plateau pressures are determined by taking the maximum of $dc/d(\ln(p))$ (The isotherm shown was measured at 353 °C and 2 SCCM).

FIG. 11. Isotherms (343 °C) of the hydrogen absorption of Mg_2Ni at a hydrogen flow of 1 and 2 SCCM. The inset shows $dc/d(\ln(p))$.

the following thermodynamic values can be calculated: $\Delta H = -62 \pm 2 \text{ kJ mol}^{-1} \text{ H}_2$ and $\Delta S = -119 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1} \text{ H}_2$. The values agree well with the literature values of $\Delta H = -64.5 \pm 4.2 \text{ kJ mol}^{-1} \text{ H}_2$ and $\Delta S = -122.2 \pm 6.3 \text{ J K}^{-1} \text{ mol}^{-1} \text{ H}_2$.² The errors from our measurements include only the statistical errors from the linear fit without considering the temperature errors due to the potential temperature gradient in the sample.

The result of a combined XRD and pcT measurement during hydrogen absorption is shown in Fig. 13. The XRD intensity is shown in an image plot as a function of the diffraction angle and the hydrogen amount. Superimposed is the corresponding adsorption isotherm ($T = 343$ °C, $f = 2$ SCCM). In order to make the low quantity of Mg and MgH_2 visible, the logarithm of the intensity is shown. At a low hydrogen amount (<0.2 wt. %) and a low pressure (<5 bars) the formation of the $\text{Mg}_2\text{NiH}_{0.3}$ α -phase is seen at the shift of the Mg_2Ni peaks to lower angles. Due to the higher stability of MgH_2 compared to Mg_2NiH_4 , during hydrogenation, the MgH_2 phase is formed out of Mg at lower hydrogen pressures (<7.5 bars) and at a low hydrogen amount (<0.5 wt. %). At higher hydrogen amount (>0.5 wt. %) the sudden formation of the Mg_2NiH_4 phase out of $\text{Mg}_2\text{NiH}_{0.3}$

FIG. 12. Van 't Hoff plot of the plateau pressures for the hydrogen absorption of Mg_2Ni . $\ln(p_{\text{des}}/p_0)$ is plotted as a function of the inverse temperature $1/T$.

FIG. 13. Combined XRD and pcT measurement of the hydrogen absorption of Mg_2Ni at 343 °C and a hydrogen flow of 2 SCCM. The pressure and the XRD pattern are shown as a function of the hydrogen amount.

is seen. Additionally, some MgO is seen by XRD. The major peaks of the different phases are indicated and labelled in Fig. 13.

IV. CONCLUSION

The design and construction of a high pressure (200 bars) and high temperature (600 °C) XRD cell was presented. Due to the big sample volume, and low internal volume of the cell, it can be used in combination with a pcT system to measure the de- and rehydrogenation properties of metal hydrides. The water cooled cell consists of an x-ray semi-transparent beryl-

lium dome and an electrical sample heater. The design and setup were simulated extensively by FEM analysis. Results thereof were validated by substantial experimental test measurements and are in good agreement. The feasibility of the system to perform simultaneous pcT and XRD measurements has been shown on the example of Mg_2NiH_4 .

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