Boesenberg, U.; Pistidda, C.; Tolkiehn, M.; Busch, N.; Saldan, I.;
Suarez-Alcantara, K.; Arendarska, A.; Klassen, T.; Dornheim, M.:

Characterization of metal hydrides by in-situ XRD

In: International Journal of Hydrogen Energy (2014) Elsevier

DOI: 10.1016/j.ijhydene.2014.02.068

Characterization of metal hydrides by in-situ XRD

Ulrike Bösenberg[a], Claudio Pistidda[a], Martin Tolkiehn[b], Nina Busch[a], Ivan Saldan[a],
Karina Suarez-Alcantara[a], Anna Arendarska[a], Thomas Klassen[a], Martin Dornheim[a,*]

[a] Institute of Materials Research, Helmholtz-Zentrum Geesthacht, Max-Planck-Straße 1, D-21502 Geesthacht , Germany.
[b] HASYLAB, Deutsches-Elektronen-Synchrotron DESY, Notkestraße 85, D-22607 Hamburg, Germany.
*Corresponding author. Tel.: +49 4152 87 2604; fax: +49 4152 87 2625. E-mail address: martin.dornheim@hzg.de (M. Dornheim).

Abstract

In-situ synchrotron radiation powder X-ray diffraction (SR-PXD) technique is a powerful tool to gain a deeper understanding of reaction mechanisms in crystalline materials. In this paper, the implementation of a new in-situ SR-PXD cell for solid-gas reactions is described in detail. The cell allows performing measurements in a range of pressure which goes from light vacuum (10^{-2} bar) up to 200 bar and temperatures from room temperature up to 550°C. The high precision, with which pressure and temperature are measured, enables to estimate the thermodynamic properties of the observed changes in the crystal structure and phase transformations.

Keywords: In-situ XRD, metal hydrides, complex hydrides, hydrogen storage

1. Introduction

The understanding of the solid-gas reactions kinetics and their dependence on the applied conditions (i.e. gas pressure and temperature) are key requirements to design novel materials for hydrogen storage purposes. In this regards, in-situ SR-PXD has been proven to be a very powerful tool to gain information on material properties and reaction kinetics. [1-5] X-ray scattering generally requires short data acquisition times and shows high penetration depths, especially for low Z materials, therefore, it is a very suitable technique for in-situ studies of chemical reactions. While upon hydrogenation and de-hydrogenation the interstitial hydrides typically show considerable changes in the unit cell volume [6], complex hydrides and Reactive Hydride Composites (RHC) show nucleation and growth of new phases with completely different crystal structures and atom arrangements [1]. The formation and stability of these new phases depend on the applied pressure and temperature conditions.

The temperature/pressure equilibrium conditions are function of the enthalpy and entropy of the reaction, in simple cases, such as MgH_2, this is determined by the enthalpy of the MgH_2 formation (-75 kJ/molH_2) [7] and the hydrogen entropy change (130 J/Kmol) [7].

In the last decades, owing to their favourable thermodynamic properties and high hydrogen capacities, the so called Reactive Hydride Composites (RHC) have been considered as possible candidates for hydrogen storage systems for mobile applications [8]. However, the hydrogen absorption and desorption reactions of these systems are rather complex. For the $LiBH_4$-MgH_2 system, in-situ SR-PXD significantly contributed to the understanding of the reaction pathway [1, 2]. In contrast, the exact reaction pathway for the $Ca(BH_4)_2$-MgH_2 system or even $Ca(BH_4)_2$ alone, is still unclear because of the number of intermediate phases and side reactions involved in the hydrogen desorption and absorption processes [9-12]. Yartys et al. [13] have demonstrated how the possibility to perform in-situ neutron diffraction analysis, acquiring simultaneously thermodynamic properties, is important for the characterization of high-pressure interstitial hydrides.

In this work, a newly-designed sample cell for in situ SR-PXD analysis and its experimental setup at Beamline D3, HASYLAB, DESY are described in detail. Owing to its fast reaction kinetics in a suitable temperature and pressure range, MgH_2 doped with Nb_2O_5 was selected for testing the setup [14-17]. The experiments carried out at several hydrogen pressures on the doped MgH_2 show, as expected, a clear dependence of the sorption temperature on the applied pressure. Quantitative analysis of the diffracted intensity relates the chemical reaction to pressure and temperature. In addition, the in-situ cell was employed for investigating the absorption reaction of the RHC system CaH_2-MgB_2 at hydrogen pressure of 120 bar and temperature of 350°C.

Although, in this work the cell was used for the study of hydrogen storage materials, it can be employed in the study of all sorts of solid-gas reactions. Due to the sensitive nature and high reactivity of the material in powder form, the cell is designed in such a way, that it can be mounted under inert atmosphere in a glove box.

2. Experimental

The used sample cell is a modification of previously developed cells used for studies of catalytic reactions using a flow of gas or liquids through a powder bed as well as studies of solid-gas reactions in metal hydrides [5, 18, 19]. A schematic drawing of the sample cell is shown in figure 1a. The implementation of the sample cell at the Beamline D3, HASYLAB, DESY is shown in figure 1b.

The cell is attached using a standard goniometer head on a Huber 4-circle diffractometer. The sample material, in this case powder, is inserted in a single crystal sapphire capillary with an outer diameter of 1.1mm (Saint Gobain Crystals), matching standard 1/16” Swagelok nuts. These sapphire capillaries can withstand temperatures up to 2000°C and pressures up to 900 bar [5], moreover, they are chemically inert and transparent to a high energy X-ray beam [20]. For our experiments the sample cell was introduced in an argon filled glove box to perform the loading of the sample under inert conditions.

To insure tightness for pressures up to 200 bar hydrogen, vespel ferrules (15% Graphite 85% Vespel® ferrules for Gas Chromatography from SGE) are used to tighten the Swagelok nuts and mounting the capillary. The gas is equally distributed on the sample from both sides using a 1/16” stainless steel tube between the two Swagelok nuts fixing the capillary. A type K thermocouple inserted into the powder bed in the capillary measures and controls (via a standard PID controller) the sample temperature during the experiment. The sample is heated using a ceramic heating element from BACH GmbH. The heating element is placed on the rails below the sample capillary and its position can be adjusted for each sample. For mounting the capillary it can be conveniently lowered and moved along the rails. Its operation is controlled by the thermocouple inserted in the powder bed via a PID control from JUMO GmbH, Fulda, Germany. The temperature program is set by using the corresponding software, where the temperature is recorded, also.

Pressures in the range from 10^{-2} to 200 bar can be applied using a stainless gas system equipped with Swagelok manual valves. The pressure is monitored and recorded using a WIKA pressure gauge (Alexander Wiegand GmbH) and the corresponding EasyCom software supplied by the manufacturer.

The measurements were carried out at the D3 Beamline at HASYLAB, DESY, Hamburg. A silicon (111) double crystal monochromator was used to select a wavelength of $\lambda = 0.5003$ Å. Diffraction data were collected using a MarCCD 165 2-dimensional detector (Marresearch GmbH). For normalization the intensity of the incident beam was measured using a NaJ-detector looking at a scatter foil.

3. Results and discussion

To illustrate the power of this method and the sample cell, measurements with magnesium hydride, catalyzed with 5 mol% Nb_2O_5 were measured under approximately 5, 10 and 15 bar hydrogen; the exact values are noted with the experiments in figure 2. In each measurement, the sample was heated up to 450°C with 5 K/min and after an isothermal period of 5 min cooled down to room temperature, also with 5 K/min. The results are shown in figure 2, a, b and c. Below the X-ray diffraction data the temperature, pressure and peak area for MgH_2 and Mg as a measure of quantity is plotted for each experiment. The pressure was measured in relative units, that means that p = 0 bar is equivalent to atmospheric pressure.

The correlation between the change in pressure and the sorption reaction is striking. As the temperature reaches the equilibrium temperature for the chosen pressure, e.g. 345°C for the experiment performed under 5 bar hydrogen pressure, immediate desorption of MgH_2 into metallic Mg can be observed. This is followed by a distinct rise in pressure of about 0.15 bar. Qualitative analysis clearly correlates the desorption reaction to a fast decrease in the intensities of the MgH_2 reflections and to a formation and increase in intensity of metallic Mg reflections. During the cooling, the opposite effect is observed. As the pressure decreases again, at a slightly lower temperature than the one of the previous desorption reaction, the intensities of the Mg reflections decrease and vanish while the up-rise of the MgH_2 reflections can be observed. For the analysis of the relative changes in the phase fractions, peak areas of the MgH_2 (110) and Mg (102) reflections were evaluated. The lack of diffraction data in the middle of the experiment at 10 bar hydrogen is due to refilling of the synchrotron storage ring.

Increasing the applied hydrogen pressure a clear increment of desorption temperatures is noted. Besides the changes in the material sorption properties, variations of the material phase composition are visible. As the measurements start from nanocrystalline MgH_2 with a mixture of β– and γ–phase, the γ-phase vanishes during the first heating and is not reformed during cooling. The decrease of the full width at half maximum of the MgH_2 intensities is caused by coarsening of the MgH_2 crystallites. It also occurs mainly during the first heating and desorption reaction but continues upon cycling at these high temperatures. Furthermore, the weak reflexes of Nb_2O_5 can be observed. The reflections remain weak with the ongoing sorption processes, indicating that the material nanostructure remains constant. Furthermore reaction between Nb_2O_5 with MgH_2 or Mg can be observed, resulting in the final formation of MgO, as previously reported by Friedrichs et al. [21].

The pressure changes in the in-situ cell caused by the heating/cooling of the sample are negletable. In fact, the overall inner volume of the in-situ cell is roughly 2 mL, whereas, the volume of the heated portion of the cell (i.e. the capillary) is only about 0.005 mL. Furthermore, as the pressure is measured continuously throughout the experiment, the pressure changes caused by the temperature changes can be subtracted as a linear baseline.

For future experiments the synchronisation of the recording system for diffraction frames, temperature and pressure will be optimized to access highly precise information.

The application of higher pressures and the investigation of more complex systems are well feasible. As an example, the first absorption reaction of the RHC system CaH_2-MgB_2 under 120 bar hydrogen and a temperature of 350°C is shown in figure 3.

As the initial CaH_2-MgB_2 material is heated, the CaH_2 peaks intensity becomes more pronounced, due to crystallite coarsening. In the isothermal period, clearly the formation of β-$Ca(BH_4)_2$ and MgH_2 can be observed. The lack of diffraction data after 1.5 hours into the experiment is due to injection at the synchrotron storage ring. The pressure is rather stable over the whole experiment, starting at 121 bar hydrogen a value of 117 bar is reached at the end of the experiment. The linear decrease by 4 bar is due to a small leakage. During the last scans of the cooling a phase transformation from β-$Ca(BH_4)_2$ to α-$Ca(BH_4)_2$ can be observed. The slow reaction kinetics in combination with the slight hydrogen-leakage do not allow tracing the absorption reaction as a decrease in pressure.

4. Conclusions

In conclusion, in-situ SR-PXD is an extremely powerful tool to investigate solid-gas reactions, e.g. hydrogen sorption reactions of metal hydrides. The ongoing reactions and phase transformations can be characterized as a function of pressure and temperature. Recording of pressure and temperature throughout the whole experiment allows for powerful conclusions on the reaction pathway and even thermodynamic properties, especially in combination with quantitative analysis. The newly implemented setup at Beamline D3, HASYLAB, DESY allows measurements in environments up to 200 bar hydrogen and 550°C.

Acknowledgements

The authors thank Klaus Pranzas, Mathias Herrmann and Dennis Heims for experimental support. The authors are especially grateful Dr. Torben R. Jensen, Aarhus University, Denmark for his help and support. Financial support of the German Chinese Sustainable Fuel Initiative is gratefully acknowledged. This work was supported by the European Community under MRTN-Contract “Complex Solid State Reactions for Energy Efficient Hydrogen Storage”(MRTN-CT-2006-035366).

Figure 1 a) Schematic drawing of the in-situ sample cell and b) its implementation at Beamline D3, HASYLAB, DESY. The insert magnifies the sample within the capillary and the heater placed beneath.

Figure 2 In-situ XRD of MgH_2 under different hydrogen pressures a) p = 5bar H_2, b) 10bar H_2 and c) 15bar H_2. Below the diffracted patterns quantitative analysis of the diffracted intensities of the MgH_2 (110) peak and the Mg (102) are plotted. Furthermore, the absolute pressure as well as the sample cell is plotted. All data are correlated to each other by measurement time.

Figure 3 In-situ XRD of an absorption reaction in CaH_2-MgB_2 composites measured at 120 bar hydrogen, holding approx. 2.5 hours isothermal at 350°C.

References

[1] Bösenberg U, Doppiu S, Mosegaard L, Barkhordarian G, Eigen N, Borgschulte A, et al. Hydrogen sorption properties of MgH_2–$LiBH_4$ composites. Acta Mater 2007;55:3951-8.

[2] Bösenberg U, Ravnsbæk DB, Hagemann H, D'Anna V, Minella CB, Pistidda C, et al. Pressure and temperature influence on the desorption pathway of the $LiBH_4$–MgH_2 composite system. J Phys Chem C 2010;114:15212-7.

[3] Gross KJ, Guthrie S, Takara S, Thomas G. In-situ X-ray diffraction study of the decomposition of $NaAlH_4$. J Alloy Compd 2000;297:270-81.

[4] Jensen TR, Andreasen A, Vegge T, Andreasen JW, Ståhl K, Pedersen AS, et al. Dehydrogenation kinetics of pure and nickel-doped magnesium hydride investigated by in situ time-resolved powder X-ray diffraction. Int J Hydrogen Energ 2006;31:2052-62.

[5] Jensen TR, Nielsen TK, Filinchuk Y, Jorgensen J-E, Cerenius Y, Gray EM, et al. Versatile in situ powder X-ray diffraction cells for solid-gas investigations. J Appl Crystallogr 2010;43:1456-63.

[6] Buchner H. Energiespeicherung in Metallhydriden. Wien: Springer; 1982.

[7] Lide DR. Handbook of Chemistry and Physics. Boca Raton: CRC Press; 1994.

[8] Dornheim M, Eigen N, Barkhordarian G, Klassen T, Bormann R. Tailoring hydrogen storage materials towards application. Adv Eng Mater 2006;8:377-85.

[9] Barkhordarian G, Jensen TR, Doppiu S, Bosenberg U, Borgschulte A, Gremaud R, et al. Formation of $Ca(BH_4)_2$ from hydrogenation of CaH_2+MgB_2 composite. J Phys Chem C 2008;112:2743-9.

[10] Kim J-H, Jin S-A, Shim J-H, Cho YW. Reversible hydrogen storage in calcium borohydride $Ca(BH_4)_2$. Scripta Mater 2008;58:481-3.

[11] Kim Y, Reed D, Lee Y-S, Lee JY, Shim J-H, Book D, et al. Identification of the dehydrogenated product of $Ca(BH_4)_2$. J Phys Chem C 2009;113:5865-71.

[12] Kim Y, Reed D, Lee Y-S, Shim J-H, Han HN, Book D, et al. Hydrogenation reaction of CaH_2–CaB_6–Mg mixture. J Alloy Compd 2010;492:597-600.

[13] Yartys VA, Denys RV, Webb CJ, Mæhlen JP, Gray EM, Blach T, et al. High pressure in situ diffraction studies of metal–hydrogen systems. J Alloy Compd 2011;509, Supplement 2:S817-S22.

[14] Oelerich W, Klassen T, Bormann R. Metal oxides as catalysts for improved hydrogen sorption in nanocrystalline Mg-based materials. J Alloy Compd 2001;315:237-42.

[15] Barkhordarian G, Klassen T, Bormann R. Fast hydrogen sorption kinetics of nanocrystalline Mg using Nb_2O_5 as catalyst. Scripta Mater 2003;49:213-7.

[16] Barkhordarian G, Klassen T, Bormann R. Patent pending. 2004.

[17] Dornheim M, Doppiu S, Barkhordarian G, Boesenberg U, Klassen T, Gutfleisch O, et al. Hydrogen storage in magnesium-based hydrides and hydride composites. Scripta Mater 2007;56:841-6.

[18] Chupas PJ, Ciraolo MF, Hanson JC, Grey CP. In situ X-ray diffraction and solid-state NMR study of the fluorination of γ-Al_2O_3 with HCF2Cl. J Am Chem Soc 2001;123:1694-702.

[19] Chupas PJ, Chapman KW, Kurtz C, Hanson JC, Lee PL, Grey CP. A versatile sample-environment cell for non-ambient X-ray scattering experiments. J Appl Crystallogr 2008;41:822-4.

[20] http://www.photonic.saint-gobain.com/sapphire-tubes-rods.aspx access date: 10/2010.

[21] Friedrichs O, Aguey-Zinsou F, Fernández JRA, Sánchez-López JC, Justo A, Klassen T, et al. MgH_2 with Nb_2O_5 as additive, for hydrogen storage: Chemical, structural and kinetic behavior with heating. Acta Mater 2006;54:105-10.