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Metal-hydrogen systems with an exceptionally large and tunable thermodynamic destabilization

Peter Ngene\textsuperscript{1}, Alessandro Longo\textsuperscript{2,3}, Lennard Mooij\textsuperscript{4}, Wim Bras\textsuperscript{3} & Bernard Dam\textsuperscript{4}

Hydrogen is a key element in the energy transition. Hydrogen-metal systems have been studied for various energy-related applications, e.g., for their use in reversible hydrogen storage, catalysis, hydrogen sensing, and rechargeable batteries. These applications depend strongly on the thermodynamics of the metal-hydrogen system. Therefore, tailoring the thermodynamics of metal-hydrogen interactions is crucial for tuning the properties of metal hydrides. Here we present a case of large metal hydride destabilization by elastic strain. The addition of small amounts of zirconium to yttrium leads to a compression of the yttrium lattice, which is maintained during (de)hydrogenation cycles. As a result, the equilibrium hydrogen pressure of \( \text{YH}_2 \leftrightarrow \text{YH}_3 \) can be rationally and precisely tuned up to five orders of magnitude at room temperature. This allows us to realize a hydrogen sensor which indicates the ambient hydrogen pressure over four orders of magnitude by an eye-visible color change.
Reversible hydrogen absorption in metals is exploited for a variety of applications, such as hydrogen storage\cite{1,2}, hydrogen sensing\cite{3,4}, rechargeable batteries\cite{2,5,6}, smart windows\cite{7,8}, hydrogen purification/separation\cite{4,9}, and catalysis\cite{9}. For most applications, it is essential to tune the temperature and pressure at which metals can reversibly absorb hydrogen. This is essentially governed by the thermodynamics of the metal–hydrogen interaction\cite{1,10}. Hence, over the past three decades, much effort has been made to tune the thermodynamics of metal–hydrogen interactions\cite{10-20}. The equilibrium temperature and pressure at which a metal can absorb and desorb hydrogen is a fundamental property of the metal which is simply described by the Van’t Hoff relation (Eq. (1), when neglecting the temperature dependence of the enthalpy and entropy).

\[
\ln \left( \frac{P}{P_0} \right) = \frac{\Delta H^0}{RT} - \frac{\Delta S^0}{R}
\]

Here, \(P_0\) is the equilibrium or plateau hydrogen pressure, \(P_0\) is the standard pressure (taken as 1 bar \(H_2\)), \(R\) is the gas constant, \(T\) is the temperature, \(\Delta H^0\) and \(\Delta S^0\) are the change in enthalpy and entropy, respectively, at standard conditions, accompanying the (de)hydrogenation reaction. The entropy change associated with entropy, respectively, at standard conditions, accompanying the (de)hydrogenation reaction. The entropy change associated with entropy, respectively, at standard conditions, accompanying the (de)hydrogenation reaction. The entropy change associated with entropy, respectively, at standard conditions, accompanying the (de)hydrogenation reaction. The entropy change associated with entropy, respectively, at standard conditions, accompanying the (de)hydrogenation reaction.

Results

The effect of Zr on the equilibrium pressure of Y–H system. Y\(_{1-x}\)Zr\(_x\), thin films were deposited on quartz substrates by co-sputtering in a RF-DC magnetron sputter system. All films are covered with Pd to prevent oxidation and to catalyze hydrogen sorption. In addition, a 5 nm Ti layer is deposited between the Y and Pd layers to prevent alloying. Gradient Y\(_{1-x}\)Zr\(_x\) thin films were deposited on a 70 × 5 mm quartz substrate in such a way that the concentration of Y and Zr varies almost linearly along the substrate, as shown in Fig. 1a. Due to the different molar volumes, the film thickness reduces by more than 50% along the sample length. Hydrogen sorption was monitored by an optical technique called hydrogenography\cite{24}. This method allows one to measure pressure-optical transmission isotherms (PTIs), which provide the same information as the typical pressure-composition-temperature (PCT) isotherms (PCIs) but with the advantage that many samples can be measured simultaneously at exactly the same conditions.

In Fig. 1b, we show the PTIs for 73 distinct points (Zr concentrations) along the sample length, starting at \(Y_{98.25}\)Zr\(_{1.5}\) and ending at \(Y_{93.25}\)Zr\(_{6.75}\). Three different optical transitions are observed during this first hydrogenation cycle. These are due to the optical changes accompanying the transitions Y \(\rightarrow\) YH\(_{1.9}\) \(\rightarrow\) YH\(_{2.1}\) \(\rightarrow\) YH\(_3\), respectively\cite{23}. The transition from metallic Y to semitransparent YH\(_{1.9}\) starts at around 5.10\(^{-3}\) mbar and is completed at around 0.15 mbar. It is immediately followed by the formation of YH\(_{2.1}\), which is slightly darker than YH\(_{1.9}\), leading to a small decrease in transmittance. The reported equilibrium pressure for the Y \(\rightarrow\) YH\(_{1.9}\) transition is \(\sim 10^{-3}\) mbar\cite{25,26}, which is much lower than what we observe here. This indicates that this phase transition is kinetically limited, as suggested by the tilted nature of the isotherm (~5 \times 10^{-3}–0.15 mbar). We also observed a similar (tilted) isotherm in a Zr-free reference sample with similar gradient in Y thickness (Supplementary Fig. 1). In contrast, the well-defined plateau pressure and flat nature of the YH\(_{2.1}\) \(\rightarrow\) YH\(_3\) shows that this transition does not suffer from kinetic limitations as in Y \(\rightarrow\) YH\(_{1.9}\). Moreover, the 0.1 mbar plateau pressure of the reference sample (Supplementary Fig. 1) fits the thermodynamic data for pure Y\cite{25}. Remarkably, the YH\(_{1.9}\) \(\rightarrow\) YH\(_3\) plateau pressure shows a profound dependence on the Zr concentration, increasing continuously from 0.3 mbar for \(Y_{98.25}\)Zr\(_{1.5}\) to 40 mbar for \(Y_{93.25}\)Zr\(_{6.75}\) (Fig. 1b). Clearly, the presence of Zr has no noticeable effect on the kinetically driven Y \(\rightarrow\) YH\(_{1.9}\) phase transitions. The decrease in width of the isotherms with increasing Zr concentration is due to a decrease in film thickness, leading to a decrease in the amount of hydrogen absorbed and hence the magnitude of the optical change. Note, also that the change in optical transmittance of Zr upon hydrogenation is negligible compared to that of Y (Supplementary Fig. 2). YH\(_3\) cannot be fully dehydrogenated to Y at moderate conditions; instead, the sample remains in the YH\(_{1.9}\) phase.

Therefore, after the first hydrogenation/dehydrogenation cycle is completed, only the YH\(_{1.9}\) \(\rightarrow\) YH\(_{2.1}\) \(\rightarrow\) YH\(_3\) transitions are observed in subsequent cycles.

Figure 1c shows the isotherms (at 25°C) for the sixth hydrogenation cycle. All isotherms show two distinct plateau pressures, one corresponding to YH\(_{1.9}\) \(\rightarrow\) YH\(_3\) and the other around 40–45 mbar due to hydrogenation of the Pd layer. The slight decrease in transmittance in ln (\(T/T_0\)) from 0 to ~0.3 at low pressures is again due to the hydrogenation within the solid solution (YH\(_{1.9}\) \(\rightarrow\) YH\(_{1.1}\)). As expected, the equilibrium hydrogen pressure for Pd \(\rightarrow\) PdH\(_3\) does not change with the Zr
concentration, while that of YH$_{2.1}$ → YH$_3$ increases from ~0.3 mbar for 1.5% Zr to 1000 mbar for ~8.7% Zr (Y$_{91.3}Zr_{8.7}$). At about 7% Zr, the plateau pressure for the YH$_{2.1}$ → YH$_3$ transition is close to that of Pd → PdH$_x$, hence the sample seems to have one long plateau pressure around this composition. Above 7% Zr, the plateau pressure for YH$_{2.1}$ → YH$_3$ is clearly higher than that of Pd → PdH, resulting in two plateaus again. In Supplementary Fig. 3, we show that Y containing about 13 atom % Zr requires up to 10$^4$ mbar for full hydrogenation to YH$_3$. However, at these high Zr concentrations, the isotherms are tilted, thereby complicating the determination of the equilibrium pressure. Possibly, part of the tilt evolves because the hydrogen pressure is increased logarithmically from 1 to 10$^4$ mbar, resulting in a higher step size at higher pressures.

To exclude any effects of the thickness gradient (Supplementary Fig. 1) and/or lateral interaction between the various compositions, we repeated the hydrogenation experiments on six separate samples (1 × 1 cm) having the same total thickness (60 nm Y–Zr layer), but different Zr concentrations (Supplementary Fig. 4). Again, we observe that the equilibrium hydrogen pressure increases with the Zr concentration. For ~13 at.% Zr, the hydrogen plateau pressure approaches 10$^4$ mbar (the limit of our equipment) as shown in Supplementary Figs. 4 and 5. Thus, the addition of only 13 at.% Zr to Y leads to about five orders of magnitude increase in plateau pressure for the formation of YH$_3$. This indicates an exponential relationship between the hydrogen plateau pressure and the Zr concentration as depicted in Supplementary Fig. 5. To our knowledge, such a strong effect of doping on the plateau pressure has never been observed before.

True thermodynamic destabilization should also lead to an increase in the equilibrium dehydrogenation pressure. Indeed, we observe this to be the case, albeit to a lesser extent (Fig. 1d). Yttrium thin films are known to exhibit a large hysteresis between the equilibrium hydrogenation and dehydrogenation pressure. This is due to first-order nature of the transition$^{27}$. Consequently, dehydrogenation experiments were conducted between 200 and 250 °C. At these temperatures, we find that the equilibrium dehydrogenation pressure $Y_{x}Zr_{1-x}H_x$ is about three times higher than for pure YH$_3$ (~30 vs. 10.5 mbar (Supplementary Fig. 1b). The asymmetry in destabilization for hydrogenation and dehydrogenation might be related to the different structural changes that occur during these processes$^{28}$. Without going in detail here, we find that the GdZr–H system exhibits similar tunable plateau pressures (Supplementary Fig. 6), showing that this effect is not limited to Y but probably extends to all the rare earth hydrides having a similar hydrogenation behavior.

The effect of Zr on the Y lattice. To understand the origin of this remarkable thermodynamic effect, we used in situ XRD measurements to gain insight into the structure of the samples at different stages: as-prepared, hydrogenated, and dehydrogenated. The as-prepared/sputtered Y is hexagonal close packed (hcp) and exhibits a preferential orientation with the Y(002) direction.

**Fig. 1** The effect of Zr on the hydrogenation pressure of Y. **a** Schematic picture of the Y–Zr compositional gradient resulting in a wedge geometry with a thickness ranging from ~38 to 80 nm on a 70 × 5 cm quartz substrate, topped by a 5 nm Ti and 30 nm Pd cap layer. **b** Pressure transmission isotherms (PTIs) during the first hydrogen absorption cycle (0–40 mbar H$_2$ at 25 °C). It shows the PTIs of 73 different Zr concentrations measured simultaneously in the thin film compositional gradient. Clearly, the pressure at which the YH$_{2.1}$ → YH$_3$ transition occurs depends on the Zr concentration. Each line in the graph represents a 0.015 at.% increase in Zr, starting from 1.5% Zr, i.e., Y$_{98.5}Zr_{1.5}$. **c** PTIs of the sample during the sixth hydrogen absorption cycle at 25 °C, starting from the dihydride state. **d** Desorption isotherm (PTIs) at 220 °C for selected Zr concentrations (Y$_{96.6}Zr_{3.4}$–Y$_{91.3}Zr_{8.7}$). Each isotherm represents a 0.38 at.% increase in Zr, starting from 3.5% Zr. Note that before dehydrogenation, the sample was first exposed to 10$^3$ mbar (10 bar) H$_2$. The steps in pressure are due to due to the logarithmic decrease in hydrogen pressure from 10$^4$ to 1 mbar.
perpendicular to the substrate (Fig. 2a). Upon hydrogenation, it transforms into fcc YH1.9–Zr and subsequently into hcp YH3. The optical transition accompanying YH1.9 → YH2.1 does not result from a structural change but from an intra-band transition within the fcc phase. The YH1.9–Zr solid solution phase is therefore simply denoted as YH2. No sign of crystalline Zr is seen in the YZr1−x thin films after preparation, hydrogenation, or dehydrogenation. However, the 2θ value of Y(002) diffraction peak increases substantially in the Y–Zr alloy. Although Y and Zr are immiscible, the high energy of the sputtering process might have enabled the formation of a metastable Y–Zr alloy or a structurally coherent Y–Zr system, as previously reported for some other alloys with a positive heat of mixing.

The increase in the Y(002) peak position implies a decrease in the lattice compression (\(\Delta V/V\)) of YH2 and the plateau pressure at the YH2 → YH3 phase transition comparing uncompressed (\(P_c\)) and compressed (\(P_f\)) YH2 thin films showing the hcp-Y(002) diffraction peak in the as-prepared, fully hydrogenated hcp-YH3 (002) and dehydrogenated YH2 (111). The position of the peak clearly depends on the Zr concentration. Note that the Y86Zr14 sample could not be fully hydrogenated to YH3 even when applying 10 bar H₂ for 24 h. The Y86Zr14 sample might have enabled the formation of a metastable Y → Zr system, as previously reported for some other alloys with a positive heat of mixing.

Relation between the relative change in molar volume (\(\Delta V/V\)) of YH2 and the plateau pressure at the YH2 → YH3 phase transition comparing uncompressed (\(P_c\)) and compressed (\(P_f\)) YH2.

\[ \ln \left( \frac{P_c}{P_f} \right) = 2 \frac{BV_{11} \Delta V}{RT} \frac{\Delta V}{V} \]  \hspace{1cm} (3)

\(P_c\) and \(P_f\) are the plateau pressure of the compressed and uncompressed system, respectively, \(R\) is the gas constant and \(T\) the temperature. This equation implies that the thermodynamics of hydrogen sorption in metal can be precisely tuned by elastic clamping. In Fig. 2c, \(\ln(P_c/P_f)\) is plotted against the relative change in molar volume (\(\Delta V/V\)) of the YH2 as a function of the Zr concentration. This plot gives a linear relationship, as expected from Eq. (3). For Y87Zr13, \(P_c/P_f\) is \(\sim 10^3\) at room temperature (Supplementary Figs. 4 and 5), which implies that a 5.0% volume compression (\(\Delta V/V\)) is expected for YH2 based on Eq. (3), using 140 GPa as the bulk modulus \(B\) of YH2 (36, 37) and \(2 \times 10^{-6} \text{ m}^2\) mol\(^{-1}\) for the partial molar volume of hydrogen. This is very close to 4.3% compression observed for the YH2 phase in this sample (Fig. 2b) and in Supplementary Table 1, which suggests that elastic compression is responsible for the thermodynamic effects observed upon Zr doping. As mentioned earlier, the Y → YH2 transition is dominated by kinetics which hinders the observation of such thermodynamic effects.

The structure of Zr within the yttrium matrix. It is intriguing to observe that this large compression of the YH2 lattice remains intact during the hydrogenation/dehydrogenation process, which involves significant structural transformations and plastic deformations. Therefore, we investigated the structure and local environment of the ZrHx and YH2 phases using in situ XAS (X-ray absorption spectroscopy). Figure 3 shows the X-ray absorption near edge spectra (XANES) and extended X-ray absorption fine structures (EXAFS) of the Zr K-edge of the samples at
different stages. As shown in Fig. 3a, the as-sputtered Zr thin film (50 nm) has spectra that are similar to that of a standard Zr reference foil, but with substantially reduced amplitudes. This suggests that the sputtered Zr film has a similar atomic arrangement as bulk Zr, but with reduced size features as expected for a 50 nm film. The difference between the Zr and YZr films is evident in Fig. 3b, which shows the Fourier transform (FT) of their EXAFS spectra. Only one first neighbor peak is seen in the YZr samples, and the amplitude of the peak is significantly lower than for the sputtered Zr thin film. This points to a reduction in the Zr–Zr coordination number in the YZr samples compared to the Zr film (Supplementary Table 2 and Supplementary Fig. 8) and suggests that in the as-deposited YZr thin films, Zr forms nanoclusters17 rather than being atomically dissolved in the Y matrix. If Zr were atomically dissolved in yttrium, Zr would see the environment of the Y cluster which has a large coherence length according to the XRD, and therefore it would have a high coordination number. Therefore, the fact that the Y lattice is compressed is not due to the formation of a dispersed Y–Zr alloy. Instead, we postulate the formation of a coherent hcp YZr system38–40 consisting of Zr clusters coherently coupled to an yttrium matrix. The fact that we do not observe a slightly expanded first shell Zr–Zr coordination distance is probably due to the small size of the clusters.

Comparing Fig. 3a, b to Fig. 3c, d reveals that hydrogenation (1.5 bar H2 at 25 °C) induces profound changes in the structure and local environment of Zr. Based on the enthalpy of formation, exposure of the sample to hydrogen should result first in the formation of YH3 and ZrH1.5 followed by the formation of YH2 at elevated hydrogen pressures31, 42. For pure Zr hydride thin film, the analysis suggests two contributions: one from a cubic (Fd3m) and the other from a tetragonal (P4mm) zirconium dihydride phase. In YZr hydride, both the Zr coordination and the Zr–Zr distance are reduced as compared to pure Zr hydride. The latter is strange, since we would expect an expanded lattice if the assumption of a coherent lattice is correct.

To resolve this issue, we looked at the XANES spectra in more detail. First, we simulated the spectrum of the hydrogenated Zr film (ZrH2) on the basis of the EXAFS data (details in Supplementary Methods section). As shown in Fig. 4a, we find that a phase mixture of 30% cubic and 70% tetragonal clusters with a 5 Å radius closely matches the observed spectrum. As shown in Supplementary Figs. 9–17, such a match cannot be obtained in a single phase sample, even if we assume very small clusters. For the YZr hydride samples, it proved to be impossible to simulate the XANES spectrum with either the cubic or the tetragonal phase or a mixture thereof (Fig. 4b). Instead, we assumed a hexagonal Zr packing with lattice parameters (a = b = 2.90 Å, c = 5.90 Å), which are similar to those derived from the Y K-edge EXAFS results of the fully hydrogenated YZr film (see Supplementary Tables 3 and 4 and Supplementary Figs. 18–20 for the XANES and EXAFS results of the Y K-edge). The 7 Å cluster was then computationally relaxed to the lowest energy minimum and the XANES spectrum was calculated for the now strongly distorted cluster. To our surprise, a reasonable agreement of the measured and calculated spectrum is thus obtained (Fig. 4c). The fact that the lattice symmetry matches that of YH3 is a strong indication for a coherent coupling of the two lattices in the hydrogenated state. Thus, we conclude that ZrH2 is forced to adopt the hexagonal symmetry of the yttrium trihydride to maintain the coherent interface at the fully hydrogenated state. Such behavior has been observed in perovskite oxide films, where for example, La0.67Sr0.33MnO3 films grown on SrTiO3 substrate assumes the symmetry of the cubic SrTiO3 at the La0.67Sr0.33MnO3/SrTiO3 interface, leading to suppression of the octahedral rotations and an elongated c-axis lattice parameter15.

**Fig. 3 Local structure analysis with XAS.** XANES spectra of (a) the as-deposited, (c) fully hydrogenated, and (e) dehydrogenated thin films. Phase uncorrected FT of the EXAFS spectra of the (b) as-deposited, (d) fully hydrogenated, and (f) dehydrogenated Zr and Y–Zr thin films. The dashed lines are the fits of the EXAFS data, and the arrows are guides to the eyes.
Upon dehydrogenation, the EXAFS data show the presence of a cubic (8-ZrH$_2$) phase in all samples. Interestingly, the Zr–Zr interatomic distances in the YZr samples are significantly larger than in the pure Zr sample (6 Å vs. 4 Å). This suggests that the fcc ZrH$_2$ lattice is expanded in order to maintain a coherent interface with the slightly larger lattice of the fcc YH$_2$ phase. Upon subsequent (de)hydrogenation cycles, the samples exhibit XANES and EXAFS spectra that are similar to Fig. 3c–f, respectively, showing that the lattice compression and microstructure of the samples are stable upon cycling. Note that the transformation from cubic to hexagonal ZrH$_x$ during hydrogenation, and vice versa during dehydrogenation, leads to a ~12–17.2% volume change. The volume expansion and contraction will lead to a significant asymmetry in the hydrogenation and dehydrogenation processes. This might be the reason for the observed differences in the plateau pressures of the hydrogenation and dehydrogenation processes. Note, also that the Y K-edge XAS results agrees with the XRD results which shows decreasing d-spacing of YH$_x$ lattice with increasing Zr concentration (see Supplementary Tables 3 and 4 and Supplementary Figs. 18–20 for the results of the Y K-edge XAS).

The results from the XRD and XAS measurements strongly indicate that the remarkable thermodynamic effect observed in this system is due to lattice compression of YH$_x$ by ZH$_x$ nanoclusters in a coherently coupled YH$_x$–ZrH$_x$ system. The driving force for such a coherent interface is the small sizes of the Zr (clusters) for which the interface energy is reduced by coherency at the expense of strain (compression) energy. It has been shown that for small particles, the strain energy due to coherency can be more than compensated by the reduction in surface energy from interfacial chemical bonding.

The large compression of the Y lattice by small amounts of Zr (4.3% compression by ~12.5 at.% Zr) is likely due to the low bulk modulus of yttrium metal (41.2 GPa, compared to 91 GPa for Zr). The compressive stress required to achieve this lattice dilation is only 1.77 GPa. However, the bulk modulus of Y increases sharply upon hydrogen absorption (up to 140 GPa for YH$_{2.25}$) thereby increasing the compressive stress to 6.02 GPa. It is also interesting that YH$_x$ can apparently accommodate up to 4.3% strain without plastic deformation. This is similar to Mg (bulk modulus = 45 GPa) which can accommodate about 5% strain at 100 °C before plastic deformation, depending on the crystal orientation of the film.

Mixtures or metastable alloys of immiscible metals have been attracting a lot of attention recently especially in catalysis because they exhibit interesting synergistic properties that are not obtainable in phase segregated mixtures. Our results demonstrate that the addition of very minute amount of immiscible elements to a metal can lead to an unprecedented effect on the hydrogen sorption properties.

Using YZr gradient films as a “hydrogen thermometer”. An example of the practical relevance of this finding is demonstrated in Fig. 5. Here we show that the hydrogen-induced optical effects in YH$_x$ can be exploited to develop low-cost hydrogen detectors based on eye-readable color changes.

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dopants, even if they are formally immiscible, can lead to unprecedented effects on the hydrogen sorption properties of metals. Of course, it remains to be confirmed that a similar effect can be attained in bulk materials as well. However, experiments performed by Asano et al. show that a similar coherency observed in MgTi thin films can be reproduced in ball-milled bulk samples. This opens a new avenue to rationally tailor the properties of metal–hydrogen systems to the desired applications. The findings might also be applicable to a wide range of reactions where intercalation into a coherent solid host lattice leads to a substantial volume change.

Methods
Sample preparation. Thin films were prepared at room temperature in a multi-target ultrahigh-vacuum (UHV) DC/RF magnetron sputtering system with a base pressure of 10−9 mbar and a deposition pressure of 0.003 mbar Ar. The Y and Zr targets have a purity of 99.999% (4N) while the other targets (Gd, Pd, and Ti) have a purity of 99.9% (3N). The deposition rate of each metal is first determined by sputtering at a fixed power for 30 min and measuring the thickness of the deposited film using stylus profilometry (DEKTAK). For the gradient samples, the position-dependent deposition rate was measured along a 70 × 5 mm quartz substrate. Y–Zr gradient samples were prepared by sputtering Y and Zr from the opposite ends of a 70 × 5 × 0.5 mm UV-grade quartz substrates at a predetermined rate, and without rotation, while the Y–Zr samples with uniform thickness and same Zr concentration where deposited on a 10 × 10 × 0.5 mm UV-grade quartz substrate, which was rotated to ensure uniform deposition. A 5–10 nm Ti layer was deposited on the Y, Gd, Zr, (or Y–Zr, Gd–Zr) layer followed by a 10–30 nm Pd cap layer, which catalyzes hydrogen desorption and absorption, and prevents oxidation of the underlying layers. The Ti layer prevents alloying of Y and/or Zr with Pd.

Structural characterization. The phase composition and microstructure of the samples were characterized by in situ XRD measurements using a Bruker D Advance (XRD) system equipped with a Co X-ray source (0.178897 nm), and an Anton Paar in situ XRD reactor. The measurements were done at room temperature while the hydrogen pressure ranged from 0.01 to 10,000 mbar. Dehydrogenation of the hydrogenated sample at room temperature is achieved by flowing a 20% O2/Ar gas mixture over the in situ cell, while at higher temperature (200–250 °C), this is achieved by gradually lowering the hydrogen pressure until it is below the plateau dehydrogenation pressure at that temperature.

X-ray absorption spectroscopy (XAS). XANES and EXAFS measurements were done at the Dutch-Belgian Beam Line (DUBBLE) at the European Synchrotron Radiation Facility (ESRF), at the Yttrium and Zirconium K-edges (17,038 and 17,998 eV, respectively). The energy of the X-ray beam was tuned by a double-crystal monochromator operating in fixed-exit mode using a Si (111) crystal pair. Static x-ray absorption spectra were collected in a "wet" cell with a He-crystallat (Oxford Instruments) at room temperature, and at 80 K to minimize the noise induced by the thermal Debye–Waller effect. The EXAFS spectra of the samples were collected at ambient temperature in fluorescence mode using a nine-element Ge detector (Ortec Inc.), whereas the spectra of Y, Zr, and Y2O3 reference foils were collected in transmission mode using Ar-filled ionization chambers. The threshold energy E0 = 0 was defined at 17,038 and 17,998 eV, respectively, for Y and Zr K-edge. Three scans per sample were measured at room temperature and at 77 K, energy-calibrated, averaged, and further analyzed using GNXAS46, 51. In this approach, the local atomic arrangement around the absorbing atom is decomposed into model atomic configurations containing 2...n atoms. The theoretical EXAFS signal χ(k) is given by the sum of the n-body contributions, χ2...n, which take into account all the possible single and multiple scattering (MS) paths between the n atoms. The fitting of χ(k) to the experimental EXAFS signal allows to refine the relevant structural parameters of the different coordination shells, the suitability of the model is evaluated by comparison of the experimental EXAFS FT with the FT of the calculated χ(k) function. The global fit parameters that were allowed to vary during the fitting procedure were the distance R(Å), Debye–Waller factor (σ2) and the angles of the γi contributions, which were defined according to the crystallographic structures used in the data analysis. 32, 33. There exist several polymeric structures of zirconium hydride with similar atomic arrangement and Zr–Zr distances, but with slightly different lattice parameters. Accordingly, it is not trivial to establish unequivocally the crystallographic structure of the ZrHx nanoclusters, and the exact H concentration in the hydrogenated structure. Hence, we considered γ1 as the Zr–H distance, γ2 as the Zr–Zr cubic enriched phase and γ3 as the Zr–Zr distance of the tetragonal ZrH2 phase.

Hydrogen sorption measurement. The thermodynamics and kinetics of hydrogen sorption in the thin films were measured using hydrogenography, 34 in transmission mode (reflection modes for the sensing experiments). This method is based on the fact that upon hydrogenation, the metal-to-insulator transition results in a substantial increase in the optical transmission of the films, with a maximum transmittance at the equilibrium plateau pressures as shown in Supplementary Figs. 1–4. This allows one to measure pressure-optical transmission isotherms (PTIs), which provide the same thermodynamic information as the typical pressure-composition-isotherms (PCI) measured for bulk metal hydrides. In this method, the amount of light transmitted or reflected by a thin film is measured as a function of hydrogen pressure at constant temperature. The normalized transmittance of the film T/T0 is related to the hydrogen concentration C and film thickness d by Lambert–Beer law.

\[
\ln\frac{T}{T_0} = \chi C_n d
\]

Here T is the optical transmission and T0 is the initial transmittance of the film in the metallic state or, in dehydrogenated films, in the YHx phase before a hydrogen pressure is applied. The samples were placed in a sample holder, and the sample holder placed in a closed cell with gas connections. The optical transmission or reflectance of the samples is measured using a white light source and a 3CCD camera. Transmission or reflection data of the samples with uniform layers are averaged across the whole sample, while for the 70 × 5 cm long gradient samples the data was only averaged in the direction perpendicular to the thickness gradient. The hydrogen pressure is gradually varied between 1 and 102 mbar using a mixture of 0.1% H2 in Ar, 4% H2 in Ar, or pure H2 at a flow rate of 20 ml min−1. Typically, the time taken for an absorption isotherm is 8.5 h per order of magnitude in H2 pressure, and in desorption 10 h per order of magnitude in H2 pressure. The pressure steps are exponentially increasing or decreasing, so as to achieve a linear increase in the chemical potential of the gas. The logarithm of the change in optical reflection ln(R/R0) or transmittance ln(T/T0) is related to the linear change in the hydrogen concentration in the Y film.

Data availability. All relevant data are available from the corresponding author on request.

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