

# Hydrogen desorption kinetics of hafnium hydride powders

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## ABSTRACT

The kinetics of hydrogen gas release from hafnium hydride are investigated by combining experiments and density functional theory. The material is a candidate neutron shield for compact nuclear reactors, where hydrogen release will lead to a degradation in moderating function. Experimentally, we have studied the decomposition of epsilon phase ( $\text{HfH}_{2-x}$ ) powders from 25 to 1000 °C using thermogravimetry and X-ray diffraction. Isochronal heating reveals 3 characteristic desorption peaks corresponding to the release of hydrogen from each phase ( $\epsilon\text{-HfH}_{2-x}$ ,  $\delta\text{-HfH}_{1.6-x}$  and  $\alpha\text{-Hf}$ ), at  $\sim 350$ , 415, and 700 °C. This is well supported by the modelling output from density functional theory. A Kissinger analysis allowed for activation energies for desorption to be calculated ( $\sim 150$  kJ/mol, 170 kJ/mol and 90 kJ/mol respectively). The peak shape and desorption rate data suggests that a second order diffusion limited reaction controls the  $\epsilon \rightarrow \epsilon + \delta$  desorption, a first order interface limited reaction controls  $\epsilon + \delta \rightarrow \delta$ , and a surface limited zeroth order reaction limits the desorption of the  $\delta + \alpha$  phases. The analysis suggests that, at least for  $\delta \rightarrow \alpha$  regime, engineering solutions for improved thermal stability should focus on reductions in surface reactivity.

## 1. Introduction

Metal hydrides are candidate materials in advanced nuclear applications where efficient neutron moderation and attenuation are required. Hydrogen effectively moderates neutrons due to low atomic mass. Zirconium and yttrium hydrides are candidates for advanced moderators in compact fission reactors because of their high volumetric hydrogen density (e.g., 6.1, and  $5.8 \times 10^{22}$  H atoms/cm<sup>3</sup>, for  $\text{ZrH}_{1.66}$  and  $\text{YH}_2$  respectively) and relatively low neutron absorption cross section for the metal species [1–7]. For high performance neutron shielding, such as in a compact tokamak fusion reactor, a high neutron absorption cross section metal is required. Hafnium hydride is a front-running candidate material [8]. It has comparable hydrogen density ( $\sim 6.4 \times 10^{22}$  H atoms/cm<sup>3</sup> for  $\text{HfH}_{1.63}$ ), and Hf provides good thermal neutron absorption and gamma radiation attenuation. For these reasons the Hf-H system has previously been proposed as a control rod material in fission reactors [9–11]. Hf-H is also a good optical hydrogen sensor, operating across 6 orders of magnitude in pressure [12].

Despite its useful material properties,  $\text{HfH}_2$  has relatively poor thermal stability compared to  $\text{ZrH}_2$ , or  $\text{YH}_2$  in terms of decomposition of

the hydride at elevated temperature. This is of particular concern in nuclear applications where high temperature thermal excursions can occur if cooling function is temporarily lost. Loss of hydrogen will lead to reduced moderating function and a significant volumetric contraction (e.g., 3.5% from  $\epsilon\text{-HfH}_{2-x} \rightarrow \delta\text{-HfH}_{1.6-x}$  and 12% from  $\delta\text{-HfH}_{1.6-x} \rightarrow \alpha\text{-Hf}$ ), which will induce cracking if significant hydrogen concentration gradients are incurred. Hydrogen gas evolution also poses safety concerns, and will degrade the material's thermophysical and mechanical properties, leading to a reduction in overall effectiveness as a neutron shield.

At atmospheric pressure, hafnium hydride has three stable phases. The equilibrium binary Hf-H phase diagram is shown in Fig. 1. We note that the phase boundaries in Fig. 1 assume one atmosphere partial pressure of hydrogen. The highest hydrogen content phase ( $\text{HfH}_{1.86-2}$ ) is the face-centred tetragonal  $\epsilon$ -phase ( $I4/mmm$ ). With decreasing H stoichiometry, the face-centred cubic  $\delta$ -phase ( $\text{HfH}_{1.6-1.78}$ ) forms ( $Fm\bar{3}m$ ). In both hydride phases hydrogen atoms sit on the tetrahedral interstitial sites. Hafnium metal forms a hexagonal close packed  $\alpha$ -phase ( $P6_3/mmc$ ), and has a hydrogen solubility up to  $\text{HfH}_{0.01}$  at room temperature, increasing to  $\sim \text{HfH}_{0.1}$  at 800 °C. At lower temperatures two meta-stable

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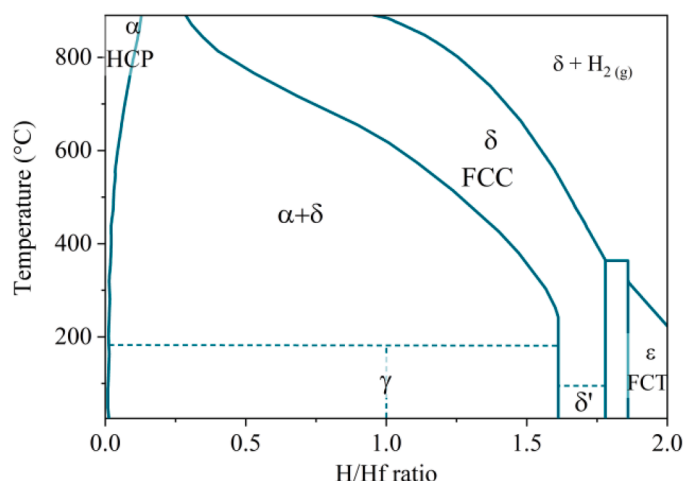
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**Fig. 1.** The binary Hf-H phase diagram where the solid lines represent the phase diagram adapted from Mintz et al. [17] and the dashed lines represent the low temperature phases adapted from Dottor et al. [14].

phases are reported. The tetragonal  $\delta'$ -phase forms below 80°C and exists in the same stoichiometric range as the  $\delta$ -phase. The  $\delta'$ -phase is a tetragonally distorted  $\delta$ -phase, whereby the H atoms sit ordered on the tetrahedral interstitial sites as the  $\delta' \leftrightarrow \delta$  is an order-disorder 2<sup>nd</sup> order transition [13–15]. Lastly, a tetragonal (PtS)-structure  $\gamma$ -phase of H/Hf=1 was recently reported to exist experimentally in the temperature range 210–150°C analogous to the Zr-H system [14,16].

As Fig. 1 shows, the  $\delta$ -phase is not stable above ~400°C under 1 atmosphere of hydrogen pressure, therefore the thermophysical properties of the  $\delta$ -phase are generally only reported up to ~300°C [18–20]. Limited decomposition data was reported by Araki et al. [21], who performed thermo-gravimetric analysis (TGA) experiments in Ar atmosphere on buttons of  $\delta$ -HfH<sub>1.6</sub> (with 0–10 at. % Zr in solid solution). Mass loss began at ~530°C regardless of Zr impurity content, but no quantitative kinetic information was reported.

More generally, for a metal hydride to desorb hydrogen when heated under low hydrogen partial pressures (or vacuum), five different processes must occur sequentially: (1) hydride decomposition; (2) hydrogen diffusion; (3) surface penetration; (4) recombination of H-H at the surface; and (5) H<sub>2</sub> desorption as gas [22]. Depending on which of these is the slowest, the isochronal desorption spectrum (i.e., hydrogen release rate vs. temperature) will have different characteristic peaks shapes, as predicted from theory in refs. [23] and [24]. For example, when limited by diffusion in the hydride phase, the peak will have a near-infinite slope on the peak ascension (left-side), and a slowly attenuating peak descension (right-side). For a reaction limited by movement of the hydride-metal interface, the peak is symmetrical. When the reaction is limited by the gas-solid surface reaction stage, the peak is asymmetric in the opposite sense to the diffusion limited case; with a slowly (and exponentially) rising left side and a sudden drop on the right side, when full-desorption is reached [24,25].

Meanwhile the position of the peaks in the thermal desorption spectra can be related to the equilibrium hydrogen pressure of metal hydride phases. The two sides of the peak correspond to the phase diagram: ascending edges (before the peak) are related to mixed phase region such as where the metal and hydride phases coexist. Whereas, the descending edges (after the peak) are representing the single-phase hydride region [26]. A diagram elucidating the interrelation of peak position and the phase evolution is shown in Supplementary figure 1. This is explained by the fact that the mixed phase region in a metal hydride pressure-composition-temperature (PCT) isotherm is flat with respect to H stoichiometry, therefore the equilibrium hydrogen pressure is a function of temperature only, hence giving rise to ascending edges in thermal desorption spectroscopy (TDS) spectra. Whereas, in the

single-phase region, the equilibrium hydrogen pressure is both a function of temperature and H stoichiometry, with the loss in H stoichiometry being the dominant factor. This causes the system to become more stable and the rate of desorption decreases leading to a descending rate in the desorption spectrum [26].

Thus, various rate limiting steps can be ascribed to metal hydride decomposition, depending on the metallic species, the hydrogen stoichiometry, the temperature and the specimen geometry. It has been reported that the  $\epsilon \leftrightarrow \delta$  phase transition is second-order in thin films [27]. However, the decomposition of these phases in bulk powder form is yet to be reported. Such information is vital to guiding the fabrication of neutron shielding components. In this study we show that the desorption occurs in three sequential stages: The first stage is limited by hydrogen diffusion with the hydrogen rich phase ( $\epsilon$ ), the second by hydrogen transfer across the interface between the shrinking  $\epsilon$ -phase and the growing hydrogen poor phase ( $\delta$ ); and the third stage by surface recombination of hydrogen atoms to form the gas. The results are consistent with the ZrH<sub>2</sub> system literature for the stages 2 and 3, but differ for stage 1, which can be explained by the significantly lower transition temperature for the reaction in the HfH<sub>2</sub> system.

## 2. Experimental

### 2.1. Materials

HfH<sub>2</sub> powder (99.9% metallic purity) was supplied by Nanochemzone and stored in a Saffron DAB01S glovebox under argon atmosphere. Powder surface area and particle size were determined by Brunauer–Emmett–Teller (BET) analysis using a Quantacrome NOVA 4000 surface area analyser, and their particle size was analysed using a Beckman Coulter LS13320 laser diffraction analyser. The tests were carried out by Metrics Ltd. Elemental analysis of the as received powders was determined using a Horiba EMGA 830 combustion analyser. Powders were placed into Ni capsules, loaded into graphite crucibles, combined with a Ni metal flux, and combusted at ~3000°C. The resulting H<sub>2</sub>O and CO<sub>2</sub>/CO signals were compared against a Y<sub>2</sub>O<sub>3</sub> standard of known oxygen content (21.256 wt.% O) and a TiH<sub>2</sub> hydrogen standard (4.04 wt.% H), which were each calibrated against three blank runs. Scanning Electron Microscopy (SEM) of the as received powder particles on carbon tape was carried out using a Zeiss Sigma 300 field emission gun SEM in Secondary Electron Imaging (SEI) mode with an accelerating voltage of 20 kV.

### 2.2. Thermogravimetry

Simultaneous Thermogravimetric Analysis/Differential Thermal Analysis (TGA/DTA) was performed using a Netzsch Jupiter STA449C. Two types of isochronal heating experiments were run: (i) variable heating rate experiments from 25–1000°C in the range 1–20°C.min<sup>-1</sup> using a Pt-Rh (K-type) thermocouple with Al<sub>2</sub>O<sub>3</sub> crucibles and ~100 mg of powder; and (ii) variable maximum temperature experiments at 1°C.min<sup>-1</sup> to a maximum temperature in the range 300–850°C using a W-Re thermocouple (W-type) with a graphite crucible and ~10 mg of powder. Some isothermal heating experiments were also performed, the data is provided in Supplementary figure 2. For each experiment HfH<sub>2</sub> powder was removed from the glovebox and weighed using a balance with accuracy to 0.1 mg. All experiments were performed under a flowing argon atmosphere of 99.9 % purity at 50 ml/min and the furnace was evacuated and refilled with argon 3 times before each experiment. The pipes connecting the gas bottle to the TGA apparatus were flexible PVC which has some oxygen permeability. The cooling rate was 40°C.min<sup>-1</sup> for all experiments. The TGA/DTA apparatus was calibrated using the melting point of metallic elements. Background correction runs were performed before each experiment with an empty crucible. Initial desorption onset temperatures were extracted using the tangent method. Due to peak overlap, peak temperatures were extracted from TGA data by taking the

3<sup>rd</sup> derivative in the mass loss and locating the peak minima (example shown in Supplementary figure 3). A data smoothing and splining function was applied to reduce noise. The TGA signals were converted into a rate of mass loss signal by taking the derivative of the TGA signal, and normalising by the BET-measured powder surface area. The resulting signal was then converted into an equivalent molar mass of hydrogen. Finally, the signal was normalised by dividing it by the heating rate to allow visual comparison of the datasets at various heating rates. The resulting units were  $\text{mol H cm}^{-2}\text{C}^{-1}$ .

### 2.3. X-ray diffraction

All X-ray diffraction (XRD) was carried out with a Cu K- $\alpha$  source ( $\lambda = 1.5406 \text{ \AA}$ ). The as-received powder and variable heating rate samples were analysed at room temperature using a Panalytical X'Pert powder diffractometer. The generator voltage was 40 kV, the current 40 mA, the scanning rate  $0.58^\circ/\text{min}$ , and the angular range  $20\text{--}90^\circ$ . The variable maximum temperature samples were analysed at room temperature on a Bruker D2 Phaser diffractometer with a generator voltage 30 kV, a current of 10 mA, a scanning rate of  $1.67^\circ/\text{min}$ , and an angular range of  $30\text{--}70^\circ$ .

High temperature XRD was performed using a Panalytical Empyrean instrument fitted with an Anton Parr environmental heating chamber. Powder was levelled on an alumina sample holder. The furnace was evacuated with a roughing pump, and back-filled three times with high purity (99.9%) nitrogen gas, and subsequently purged with nitrogen for the remainder of the experiment at a flow rate of 4 ml/min. The heating rate was  $20^\circ\text{C}/\text{min}$ , with dwell periods for data collection at 25, 300, 380, 420, 460, 520, 580 and  $600^\circ\text{C}$ . Equivalent measurements were also taken upon cooling. The generator voltage was 40 kV, the current 40 mA, the scanning rate  $5.3^\circ/\text{min}$ , and the angular range  $30\text{--}70^\circ$ .

Peak positions were obtained by fitting a pseudo-Voigt peak function in the HighScore+ software. The resulting peak positions were then indexed and compared with those present in the JCPDS database via the International Centre for Diffraction Database. Lattice parameters were calculated using the Unit Cell software package.

### 2.4. Density functional theory calculations

The calculations were performed using the Vienna Ab initio Simulation Package (VASP), where the inter-atomic force constants were calculated using the first-principles projector augmented wave (PAW) method [28], with the generalised gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) exchange-correlation functional [29]. The calculations were completed using  $2 \times 2 \times 2$  supercells of  $\text{HfH}_{2-x}$  and Hf, performed with a  $5 \times 5 \times 5$  k-point mesh with a plane wave energy cut-off of 650 eV.

Special quasi-random structures (SQS) were used to simulate the randomisation of hydrogen vacancies within the  $\text{HfH}_{2-x}$  system using the Alloy Theoretic Automated Toolkit (ATAT) [30]. This applied Monte-Carlo selection to the hydrogen lattice sites, producing the  $2 \times 2 \times 2$   $\text{HfH}_{2-x}$  supercells for a range of ratios of H/Hf: 1.97, 1.94, 1.90, 1.69, 1.65, 1, 0.5.

The Phonopy software was applied to calculate the forces acting on the atomic positions using density functional perturbation theory, determining the vibrational entropy of each of the stoichiometries [31, 32]. The phonon interactions produce the zero-point energy values for each of the systems modelled, which were subsequently used in all thermodynamic calculations providing an energy correction for the density functional theory (DFT) calculations to coincide with the experimental data.

## 3. Results

### 3.1. As received powder characterisation

Fig. 2 shows an XRD scan of the as-received powder where peaks are labelled with the corresponding phase. The major phase is  $\epsilon\text{-HfH}_{1.98}$  (04-002-3907) and the minor phase  $\alpha\text{-Hf}$  (04-004-7632). The presence of  $\alpha\text{-Hf}$  suggests the powders are not at equilibrium. The corresponding lattice parameters for the hydride phase ( $\epsilon\text{-HfH}_{1.98}$ ) are  $a = 3.469 \text{ \AA}$  and  $c = 4.349 \text{ \AA}$  ( $c/a$  ratio = 1.254) with a volume of  $52.3 \text{ \AA}^3$ , which shows excellent agreement to  $\epsilon\text{-HfH}_{1.98}$  ( $a = 3.461$ ,  $c = 4.395$ ,  $V = 52.65 \text{ \AA}^3$ ) in ref. [33]. The average oxygen content from combustion analysis of the as received  $\text{HfH}_2$  powder was 0.23 wt% (0.009 at.%) and the hydrogen content was 1.068 wt.% (0.66 at.%) which corresponds to a stoichiometry of H/Hf = 1.93. This hydrogen stoichiometry is below the value of 1.98 in ref. [33], which is likely the cause of the slightly smaller unit cell volume.

Fig. 3a shows the particle size analysis data, revealing a bimodal size distribution with peaks at  $5.6 \mu\text{m}$  and  $36 \mu\text{m}$ , and a third shoulder peak at  $15\text{--}20 \mu\text{m}$ . The surface area of the powders was  $0.415 \text{ m}^2\text{g}^{-1}$  and the average particle size was  $7.4 \mu\text{m}$ . Looking at the SEM images (Fig. 3b) there is evidence of powder particle agglomerates, one of which is shown in the magnified inset. This indicates that the peak at  $36 \mu\text{m}$  is due to agglomeration of particles. The images also show parallel bands of alternating light and dark contrast within a single particle, which are assumed to be twins, as observed for  $\epsilon\text{-ZrH}_2$  [34].

### 3.2. Dynamic TGA experiments

Fig. 4a shows the dynamic TGA results. Mass loss is displayed as a function of temperature at various heating rates in the range  $1\text{--}20^\circ\text{C}/\text{min}$ . The initial temperatures for desorption ( $T_{\text{des}}$ ), which are reported in the lower-left of the figure as  $T_{\text{des}}$ , increased with heating rate from  $260^\circ\text{C}$  at  $1^\circ\text{C}/\text{min}$  to  $298^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$ . Several steps are present in the mass loss curves between about  $300^\circ\text{C}$  and  $800^\circ\text{C}$  as shown by changes in the gradient, indicating different desorption processes are occurring sequentially. Heating rates below  $10^\circ\text{C}/\text{min}$  led to a small amount of mass gain above  $700^\circ\text{C}$  due to some powder oxidation, while for heating rates of  $10^\circ\text{C}/\text{min}$  and above the mass loss was monotonic. The mass loss signal in Fig. 4a is converted to H/Hf ratio in Fig. 4b. This is done by assuming that all mass loss is from hydrogen desorbed from

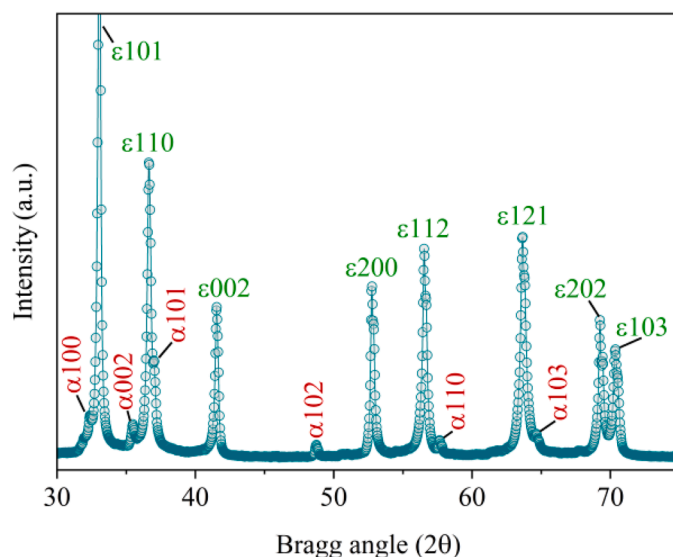
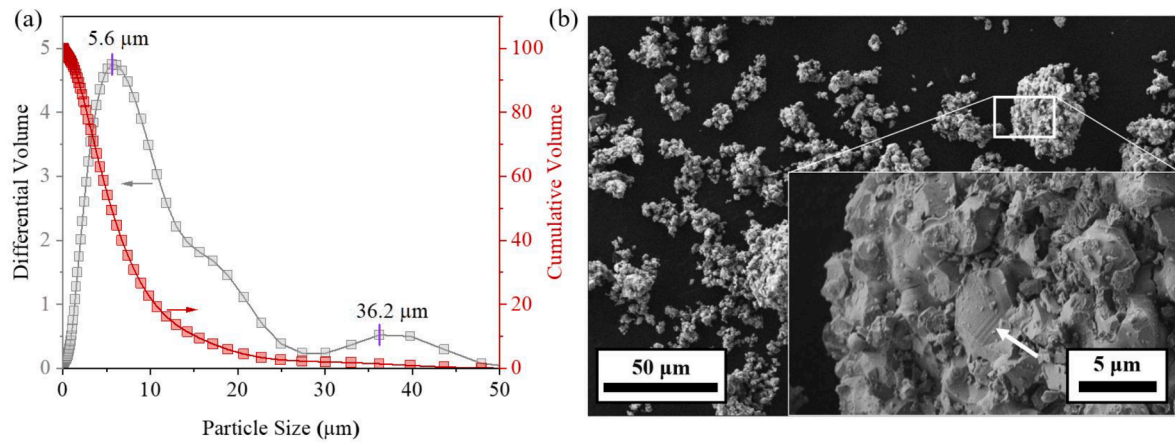
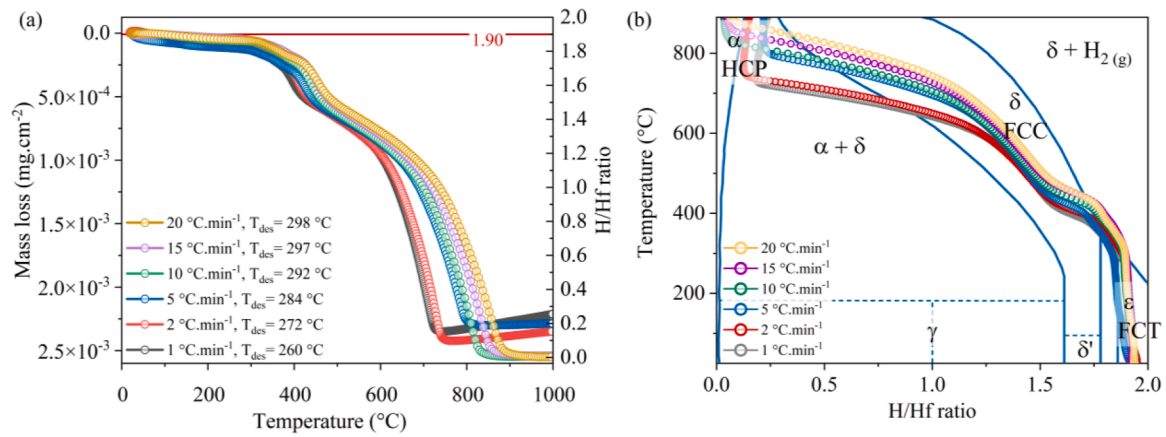


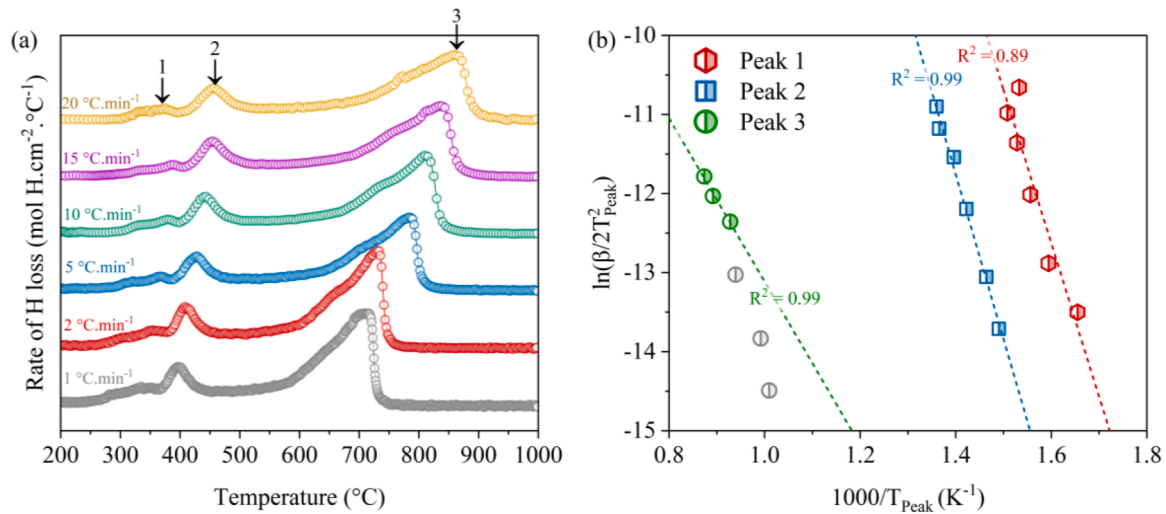
Fig. 2. XRD of the as-received powder, showing the majority is the tetragonal  $\epsilon\text{-HfH}_{1.98}$  (green), with a minor amount of hexagonal  $\alpha\text{-Hf}$  (red) where the peaks relating to each phase are indexed.



**Fig. 3.** As received  $\text{HfH}_2$  powder characterisation showing bimodal particle size a). Particle size distribution b). SEM micrographs showing particle agglomerates (inset) and twinning microstructure (arrow).



**Fig. 4.** a) TGA data showing  $\text{HfH}_2$  decomposition at 1, 2, 5, 10, 15 and  $20\text{ }^\circ\text{C.min}^{-1}$  heating rates. The secondary axis shows the conversion of the mass loss signal into the H/Hf stoichiometry as per Eq. (1). The initial desorption temperature ( $T_{\text{des}}$ ) is listed next to the respective heating rate. b) Mass loss data at all heating rates converted to H/Hf ratio and overlaid over the binary Hf-H phase diagram.



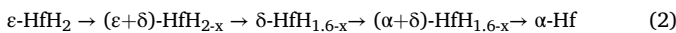
**Fig. 5.** a) Rate of hydrogen desorption from TGA measurements at different heating rates. The arrows on the  $20\text{ }^\circ\text{C.min}^{-1}$  show the approximate locations of the peaks 1, 2, and 3 from left to right. b) Kissinger analysis of the peaks extracted from the rate of hydrogen desorption. The activation energies calculated for the respective peaks are  $161 \pm 26$ ,  $173 \pm 7$ , and  $86 \pm 9\text{ kJ.mol}^{-1}$  for the peaks 1, 2 and 3 respectively. For peak 3, the slow heating rate data is discounted (and shown in grey) due to the onset of oxidation above  $700\text{ }^\circ\text{C}$ .

the material via the reaction:



Fig. 4b shows that the change in H/Hf ratio measured by TGA for the faster heating rates (10, 15 and 20°C.min<sup>-1</sup>) was 1.90 ± 0.003. Heating rates below 10°C.min<sup>-1</sup> gave values of ~1.7 or less due to the artificial increase in H/Hf ratio above 700°C, as a result of oxidation. This is due to the prolonged exposure times at temperatures above 700°C (5 hours for the 1°C.min<sup>-1</sup> sample vs. only 15 minutes for the 20°C.min<sup>-1</sup> sample). The longer exposure at slower heating rates led to significant oxidation. This was confirmed visually by a progressive discoloration of the powders from grey to white, as the heating rate decreased. The total mass loss measurements from these samples can therefore be discounted. The average ratio of 1.90 from the faster heating rate data lies close to the figure from the combustion analysis (H/Hf=1.93).

Also shown in Fig. 4b are the phase diagram boundaries taken from Fig. 1. This allows the desorption pathway to be tracked through four phase boundaries corresponding to the four transitions that will be taking place upon total desorption of the material:



To gain a better understanding of how the phase boundaries and TGA data are related, the derivative of the TG signal (DTG) is taken, which represents the rate of hydrogen loss. This DTG signal is shown in Fig. 5a. A characteristic signal containing three peaks can be seen across all heating rates (labelled 1-3 with arrows in Fig. 5a). Peaks 1 and 3 had overlapping shoulder peaks to their immediate left, with no clear maxima. This characteristic shape is mirrored by 3 clear endothermic peaks (again with smaller shoulder peaks to the left of 1 and 3) in the DTA signal, as shown in Supplementary figure 4. The DTA peaks are endothermic as energy is needed to break the metal-hydrogen bonds [35], giving further confirmation that the peaks are resulting from hydrogen desorption.

Peak 1 is minor in intensity and occurs between 300 and 350°C, depending on the heating rate. There is then a small valley in the DTG before peak 2 begins. Peak 2 forms a more symmetric shape which is higher in intensity, occurring in the range 400-450°C. This is then followed by a wide valley in the DTG plot in the temperature range 450-650°C. Peak 3 exhibits the greatest intensity and occurs at 650-750°C. It is highly asymmetric; increasing exponentially until the material has completely decomposed, after which the peak drops sharply to zero. At higher heating rates the shoulder becomes more prominent. The two shoulder peaks on peaks 1 and 3 are likely to be a consequence of the bimodal particle size distribution shown in Fig. 3, with the smaller mono-particles desorbing at lower temperature than the agglomerated particles. The peaks show broadening as the heating rate increases; this can be explained by the fact that, at such high heating rates, larger particles will tend to develop gradients in hydrogen concentration within the particle (a point explored quantitatively in Section 4.2), leading to higher hydrogen concentrations at the centre of the particles compared to their periphery.

Based on the peak temperatures determined from Fig. 5a, a Kissinger analysis was performed to evaluate the activation energies of the hydrogen desorption processes using the equation [36,37]:

$$\ln\left(\frac{\beta}{2 \cdot T_{\text{peak}}^2}\right) = -\frac{E_{\text{act}}}{R \cdot T_{\text{peak}}} + \ln\left(\frac{A \cdot R}{E_{\text{act}}}\right) \quad (3)$$

where  $\beta$  is the heating rate in K.s<sup>-1</sup>,  $E_{\text{act}}$  is the activation energy,  $R$  is the gas constant and  $A$  is a pre-exponential factor. The Kissinger analysis is shown in Fig. 5b, showing apparent activation energies of 161 ± 26, 173 ± 7, 86 ± 9 kJ.mol<sup>-1</sup> for peaks 1, 2, and 3 respectively. Due to the excessive oxidation of samples during the slower heating rates only the 10, 15 and 20°C.min<sup>-1</sup> were used to calculate the activation energy for peak 3. The lower heating rate data is included for peaks 1 and 2, which

were less intense and hence required more data points to improve measurement accuracy. The overall shape of the peaks are in good agreement with repeat measurements using the tungsten furnace (see Supplementary Figure 5).

### 3.3. Interrupted XRD analysis

As suggested by Ref. [26], peaks in the TGA signal represent transitions from a two phase region to a single phase region whereas valleys indicate the reverse transition. Therefore, expression (2) predicts only two peaks, and 2 valleys in the desorption signal, whereas the data in Fig. 5 clearly showed three peaks. It was therefore necessary to perform interrupted heating experiments to determine the physical nature of each peak. For each experiment a fresh batch of as-received powder was used. The powder was heated at 1°C.min<sup>-1</sup>, stopped at the designated interruption temperature, and cooled immediately so that the phases could be identified by XRD. DTG curves of the experiments that were interrupted at temperatures in the range 300-650°C are shown in Fig. 6a, where the same characteristic shape as Fig. 5a is shown. The corresponding XRD measurements, taken at room temperature, are plotted in Fig. 6b. The XRD shows that at 300°C (immediately below peak 1) only  $\varepsilon$ -phase is present. Passing through peak 1 (340-380°C), the  $\varepsilon$ -phase gradually decreases in intensity as the  $\delta$ -phase begins to precipitate. This confirms that peak 1 is representative of desorption from the  $\varepsilon$ -phase via the reaction:  $\varepsilon\text{-HfH}_2 \rightarrow (\varepsilon+\delta)\text{-HfH}_{2-x} + \frac{x}{2}\text{H}_2$ .

At 420-480°C the  $\varepsilon$ -phase has disappeared, with only the  $\delta$  and  $\delta'$  phases present. These temperatures correspond to just after peak 2 in the DTG curve as the signal begins to decrease into the wide valley. Due to the XRD measurements taking place at room temperature the metastable tetragonal  $\delta'$  phase precipitates from the  $\delta$ -phase upon cooling below 83°C, as detailed in [15]. The second peak can therefore be deduced to be related to the  $(\varepsilon+\delta)\text{-HfH}_{2-x} \rightarrow \delta\text{-HfH}_{1.6-x}$  phase transition. Where the ascending edge relates to the  $(\varepsilon+\delta)$  mixed phase region and the descending edge (after the peak) relates to the single phase  $\delta$ -region.

Next, in the range 520-650°C a wide valley in the DTG is observed, leading up to just before peak 3. The interrupted XRD plots show the  $\alpha$ -phase growing in intensity while the  $\delta$ -phase shrinking. Also present in this temperature range are peaks at ~38 and 66°, which are likely metastable  $\gamma$ -phase formed again when cooling below 200°C (corresponding to H/Hf = 1) [14]. Overall, the data suggests that the  $\delta\text{-HfH}_{1.6-x} \rightarrow (\alpha+\delta)\text{-HfH}_{1.6-x}$  transition is occurring as peak 3 is approached.

Finally, at 850°C, peak 3 has been fully passed. The DTG signal drops sharply down as the small amount of hydrogen in solution of the  $\alpha$ -Hf phase desorbs and only  $\alpha$ -Hf remains as shown by the XRD pattern. This confirms that peak 3 represents the  $(\alpha+\delta)\text{-HfH}_{1.6-x} \rightarrow \alpha\text{-Hf}$  transition. In summary, the interrupted XRD study confirms the decomposition pathway occurs as follows:

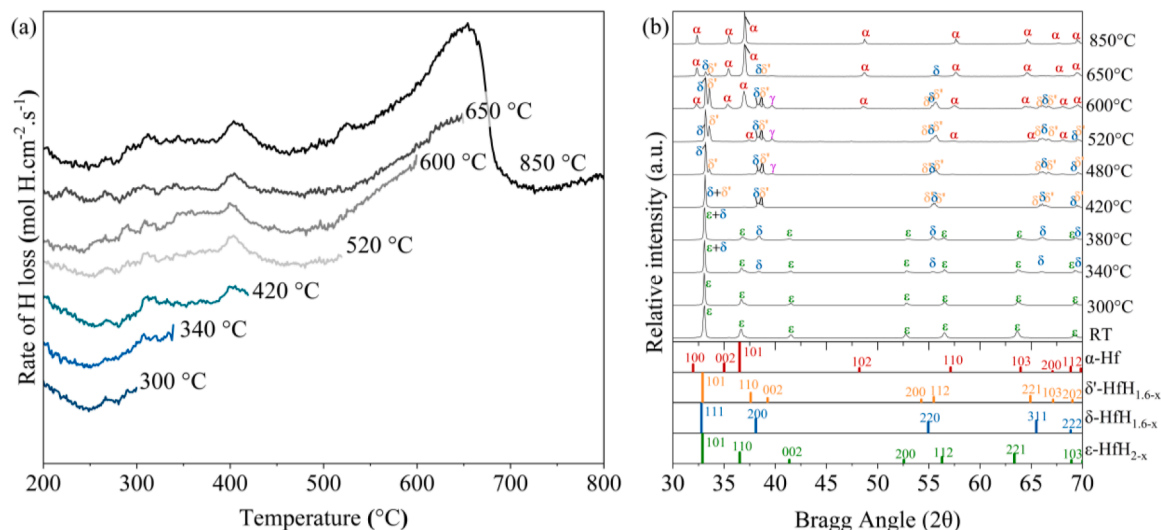
peak 1.  $\varepsilon \rightarrow (\varepsilon+\delta)$

peak 2.  $(\varepsilon+\delta) \rightarrow \delta$

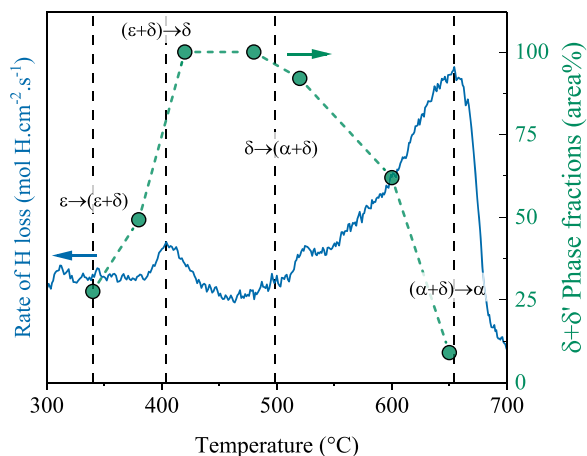
peak 3.  $\delta \rightarrow (\alpha+\delta)$ .

The mechanistic understanding developed in Figs. 4-6 can be summarised in Fig. 7. The primary y-axis (blue) shows the mass loss curve at a heating rate of 1°C.min<sup>-1</sup> from Fig. 6a, while the secondary y-axis (green) shows the  $\delta+\delta'$  phase fraction taken from the XRD data in Fig. 6b. Finally, the vertical lines show the temperatures of the phase transitions predicted by the phase diagram plot in Fig. 4b. The construction confirms the physical processes developed from the interrupted XRD analysis more intuitively.

Fig. 8 shows the lattice parameters for each phase after the temperature interruption experiments. The data for the  $\varepsilon$  and  $\delta$ -phase were fit with structures 04-002-3907 [33] and 01-089-4070 [39] from the ICDD, respectively. The lattice constants are given in Supplementary



**Fig. 6.** a) DTG curves for interrupted experiments at a heating rate of 1 °C.min<sup>-1</sup>. The maximum temperature is labelled to the right of each signature b) room temperature XRD measurements of the HfH<sub>2</sub> powder after the interrupted TGA, again with temperature indicated to the right, and indexed phases labelled with symbols. Reference patterns collected from [33,38].



**Fig. 7.** Summary of the desorption pathway comparing the rate of H loss spectra to the interrupted XRD study. The  $\delta$  phase fraction is given by the sum of the areas under the peaks in Fig. 6b for each phase as a% of the total intensity (green circles). The hydrogen loss data at 1 °C.min<sup>-1</sup> comes from Fig. 6a. The vertical lines represent the approximate locations of the phase transitions (shown by the symbols).

table 1. Figure 8a shows the data for the  $\epsilon$ -phase region. Despite the variation in hydrogen stoichiometry being minimal within the  $\epsilon$ -phase field (1.93→1.78), there is a significant change in lattice parameters. It is interesting to note that the c-axis expands, while the a-axis contracts, with increasing temperature. Fig. 8b shows the lattice parameter values for the  $\delta$ -phase as a function of H/Hf ratio. This ratio was calculated following the same analysis procedure as that shown in Fig. 4b. The data can be well fit with a linear expression, which has a similar gradient to that reported by Ref. [14] for hafnium deuteride in the  $\alpha$ + $\delta$  region. Previous studies on sieverts produced  $\delta$ -HfH<sub>x</sub> samples by Ito and Berant showed a very steep linear relationship between lattice parameter and H/Hf ratio within the single-phase  $\delta$  region. This is because in the single-phase region, changes in hydrogen content directly change the stoichiometry of the  $\delta$  phase. Whereas in the two-phase region, additional hydrogen primarily increases the volume fraction of  $\delta$ -phase.

### 3.4. High temperature X-ray diffraction

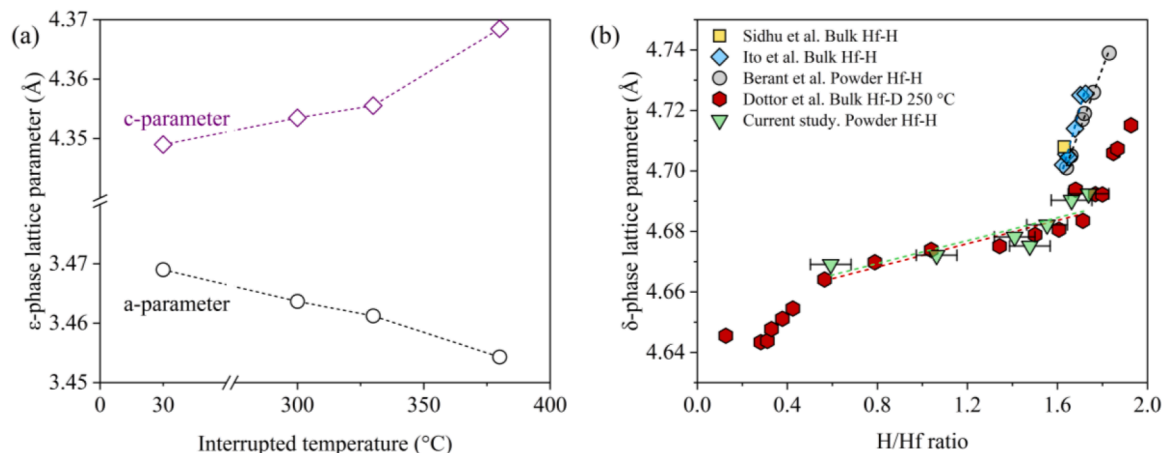
Fig. 9 shows the high temperature X-ray diffraction (HTXRD) data in the region of the  $\epsilon$ → $\delta$  phase transition. The data has been separated into a 35.5–42.5 ° region (part a) and 51.5 to 57 ° (part b) for clarity. For the  $\epsilon$ -phase, between 25 and 300 °C the peak positions have shifted due to thermal expansion, and the intensity of all the  $\epsilon$ -HfH<sub>2</sub> phase peaks remains unchanged. Above 300 °C, however, the intensity of these peaks decreases due to the onset of hydrogen desorption. The peak positions also continue to shift: the (002) and the (112) peaks shift to the left, which indicate that the [c] axis is expanding. However, the (110) and (200) peaks shift to the right, indicating that the [a] axis is contracting. The trends follow Fig. 8a however more work is needed to separate the effects of temperature and hydrogen loss. As the  $\epsilon$  peaks attenuate, there is growth in the (220) and (200) peaks of the  $\delta$ -HfH<sub>2-x</sub> phase. In contrast to the  $\epsilon$  phase, there is relatively little change in lattice parameter in the  $\delta$  phase. This is likely because thermal expansion is counteracted by a loss in hydrogen content. The phase transition occurs over the temperature range 460–500 °C, which shows good agreement with the position of peak 2 in Fig. 5a, particularly the 20 °C.min<sup>-1</sup> data which had the same heating rate as HTXRD experiments.

The lattice parameters extracted from the peak positions for the tetragonal  $\epsilon$ -phase are presented in Fig. 10. This shows the anisotropy in the lattices response to elevated temperature, where the [a] axis contracts and the [c] axis expands. The [c] axis expansion is an order of magnitude larger than the [a] axis contraction, therefore the volume increases overall.

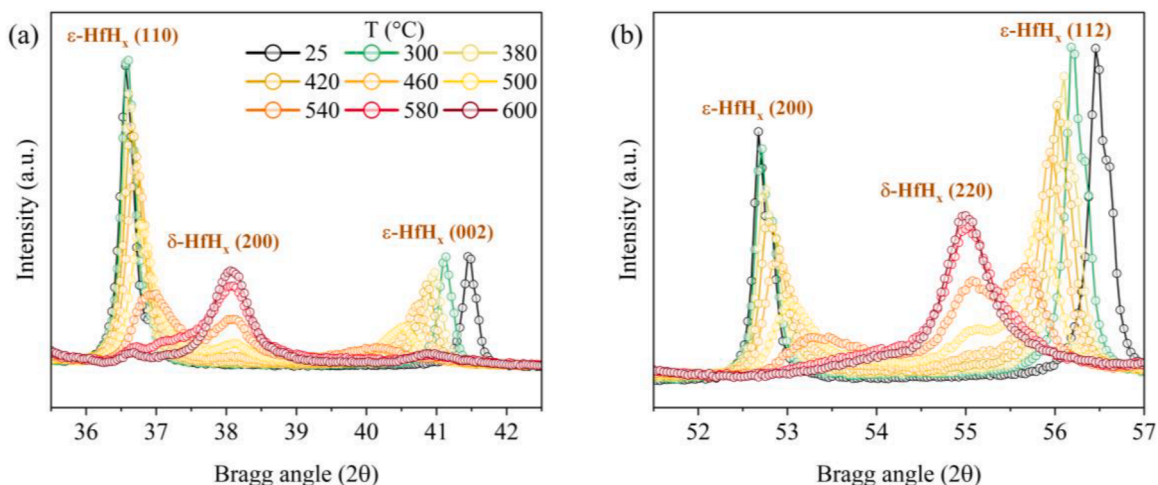
### 3.5. Computational temperature determination

Density functional theory (DFT) was applied to determine the theoretical temperatures of the transitions present across the HfH<sub>2-x</sub> system as hydrogen is released by evaluating the temperature at which the Gibbs free energy ( $\Delta G$ ) becomes < 0 eV (Supplementary figure 6). Four equations detailing the  $\epsilon$  and  $\delta$ -phases losing hydrogen were used. Where hydrogen loss without phase transformation i.e. no change in crystal structure, were considered. Additionally, phase transitions leading to structure changes and H loss are also presented. The temperature for which  $\Delta G < 0$  eV for the  $\epsilon$  and  $\delta$ -phases are overlaid onto the 1 °C.min<sup>-1</sup> data in Fig. 11.

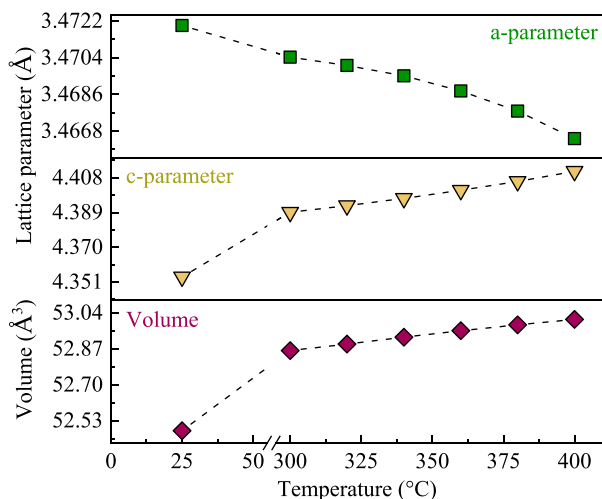
The initial computation was applied to determine the temperature in which the initial vacancy in the HfH<sub>2</sub> ( $\epsilon$  phase) occurred, forming HfH<sub>2-x</sub>,



**Fig. 8.** a) Lattice parameters for the tetragonal  $\epsilon$ -phase in interrupted samples vs. temperature (covering H/Hf ratio 1.8–1.9) showing the strongly anisotropic lattice parameter change. b) Lattice parameter for the cubic  $\delta$ -HfH<sub>x</sub> phase vs. H/Hf ratio (covering the temperature range 340–600 °C). Also shown is literature data in the two phase ( $\alpha$ + $\delta$ ) region (red pentagons < H/Hf = 1.6) and the single phase region (grey circles, blue diamonds and yellow square) [14,19,33,40]. Error bar is generated from the uncertainty in the TGA balance, as determined from repeat measurements.



**Fig. 9.** HTXRD plots of the  $\epsilon$ -HfH<sub>2-x</sub> to  $\delta$ -HfH<sub>2-x</sub> phase transition a) from 35.5 to 42.5 ° and b) from 51.5 to 57 ° at room temperature and after each heating step 300–600 °C.



**Fig. 10.** Lattice parameters for the tetragonal  $\epsilon$ -HfH<sub>2-x</sub> phase from HTXRD experiments showing the contraction in the a-parameter and expansion of the c-parameter leading to overall volume expansion as a function of temperature.

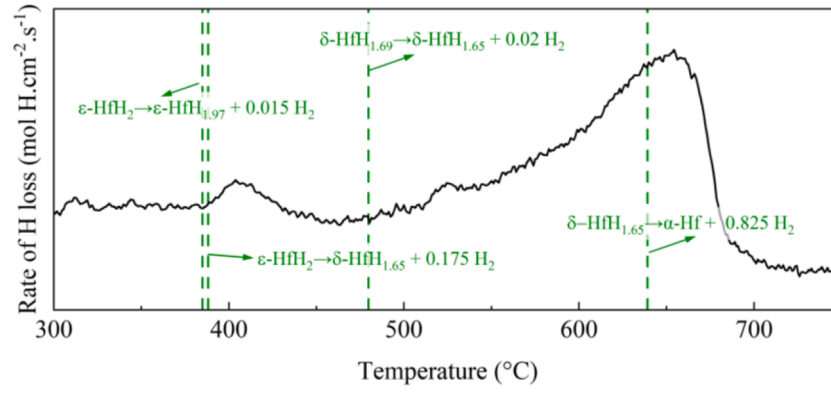
following reaction:



This calculation showed that the free energy of the reaction became 0 eV (i.e. favourable) at 384.8 °C. This value aligns well with the onset of the first large peak observed at the slower ramp rates reported in Fig. 4a (~370–390 °C). This indicates that the  $\epsilon$ -HfH<sub>2</sub> will decompose readily, however, this does not involve a change in structure. The  $\epsilon$ -HfH<sub>2</sub> to  $\delta$ -HfH<sub>2-x</sub> transition was subsequently investigated, following the reaction:



This assesses the propensity for the hydrogen to be released, forming the  $\delta$ -HfH<sub>2-x</sub> phase. The temperature at which the reaction for decomposition to the sub-stoichiometric composition was reported to proceed is 388.1 °C. This also aligns with the onset of the first large peak (~400 °C) upon heating occurring at a slightly higher temperature indicating that the phase will become non-stoichiometric in the  $\epsilon$ -HfH<sub>2</sub> structure before transitioning to the  $\delta$ -HfH<sub>2-x</sub> structure. This indicates that there is only a small window whereby the  $\epsilon$ -structure accommodates deviations in stoichiometry before transforming to the  $\delta$ -structure, this is consistent



**Fig. 11.** Computationally determined hydrogen desorption phase transition temperatures (dashed vertical lines, corresponding to the relevant equation) plotted against the experimental rate of mass loss curve at a heating rate of 1 °C.min<sup>-1</sup> to 850 °C from Fig. 6a.

with the interrupted XRD data in Fig. 6b as well as the findings by Dottor et al. detailing the  $\delta \rightarrow \epsilon$  hydrogenation reaction [14]. Then, the propensity for non-stoichiometry variation in the  $\delta$ -HfH<sub>2-x</sub> phase was determined, following the equation:



The temperature reported for this hydrogen desorption is 479.7 °C, which falls between the two major peaks in the experimental  $\delta$  desorption region where there is a slight gradient in the DTG data, coinciding with the onset of hydrogen release in the higher temperature regime. This indicates that the  $\delta$ -HfH<sub>2-x</sub> phase will continue to release H<sub>2</sub> as temperature increases. The final transition calculated was the  $\delta$ -HfH<sub>2-x</sub> to  $\alpha$ -Hf transition, given by the equation:



Whereby all hydrogen in the HfH<sub>2-x</sub> had been released (although a transition region with  $\delta$ -HfH<sub>2-x</sub> and  $\alpha$ -Hf is expected) to gain an understanding of the  $\delta$ -HfH<sub>2-x</sub>  $\rightarrow$   $\delta$ -HfH<sub>2-x</sub> +  $\alpha$ -Hf transition. This corresponded to a temperature of 639.1 °C, comparable to the reaction occurring within the third peak, indicating that this region is associated with the formation of  $\alpha$ -Hf which aligns with the interrupted XRD analysis. Overall, the temperatures calculated from DFT calculations are supportive of the experimentally derived desorption stages. These reactions do not consider kinetics, but match well with the onset of release, which largely negates the kinetic component of H loss. Considering this, the various regimes of H loss are well predicted by the models and provide a predictive tool for further analysis.

Computationally, the activation energies of hydrogen desorption in each of the phases was calculated through the nudged elastic band (NEB) method. For the  $\epsilon$ -HfH<sub>1.97</sub> phase with hydrogen moving into a vacancy (associated with the desorption [Eq. 4]) the activation energy was calculated to be 154 kJ.mol<sup>-1</sup>, which aligns with the experimentally measured activation energy of peak 1 of 161 ± 26 kJ.mol<sup>-1</sup>. Calculating the activation energy of the  $\delta$ -HfH<sub>2-x</sub> formation from  $\epsilon$ -HfH<sub>2</sub> is computed to be 176 kJ.mol<sup>-1</sup>, which supports peak 2's experimentally determined activation energy of 173 ± 8 kJ.mol<sup>-1</sup>. Finally, the hydrogen interstitial in  $\alpha$ -Hf from  $\delta$ -HfH<sub>2-x</sub> is calculated as 148 kJ.mol<sup>-1</sup>, which is significantly higher than the measured activation energy of 86 ± 9 kJ.mol<sup>-1</sup>. These activation energies are associated with mobility of hydrogen within the crystal structure, and do not consider mobility along other features including grain boundaries and dislocations. Despite this the values are in good agreement with the experimental observations.

## 4. Discussion

### 4.1. Rate limiting mechanism

In Section 3.3 we determined the phase transformation responsible for each peak in the desorption spectrum. We now address the mechanism that limits the overall rate of each transformation. The role of hydrogen diffusion is discussed first. H diffusion rates in Hf-H have been previously studied by Gottwald et al. [41], who reported activation energies,  $E_{\text{act}}$ , of 61 and 69 kJ.mol<sup>-1</sup> and pre-exponential factors,  $D_0$ , of  $2.8 \times 10^{-7}$  and  $3.9 \times 10^{-7}$  m<sup>2</sup>/s for HfH<sub>1.71</sub> and HfH<sub>1.94</sub> respectively. From this data the diffusion rate of H in m<sup>2</sup>/s for the  $\epsilon$  and  $\delta$  phases can be calculated using:

$$D = D_0 \cdot \exp\left(\frac{-E_{\text{act}}}{R \cdot T}\right) \quad (8)$$

where  $R$  is the gas constant ( $1.381 \times 10^{-23}$  J.K<sup>-1</sup>.mol<sup>-1</sup>) and  $T$  is the temperature (K). The characteristic diffusion time of H from the centre of a particle to the periphery can be estimated to a first-order as:

$$\tau_{\text{diff}} = r_p^2 / D \quad (9)$$

where  $r_p$  is the average particle radius ( $\sim 3.5$   $\mu\text{m}$ ) and  $D$  is the diffusion

**Table 1**

Diffusion and desorption times calculated from Eq. [9] and [10]. Diffusion data for peak 1 assumed a composition of HfH<sub>1.94</sub>, and for peaks 2 and 3 assumed HfH<sub>1.71</sub>. Diffusion data was taken from Gottwald [41] and all particles were assumed to be 3.5  $\mu\text{m}$  in radius.

| Peak | Phase transition                           | Heating rate, $\beta$ (°C.min <sup>-1</sup> ) | Peak temp. (°C) | D (m <sup>2</sup> /s)  | $\tau_{\text{diff}}$ (s) | $\tau_{\text{des}}$ (s) | $\tau_{\text{diff}}/\tau_{\text{des}}$ |
|------|--------------------------------------------|-----------------------------------------------|-----------------|------------------------|--------------------------|-------------------------|----------------------------------------|
| 1    | $\epsilon \rightarrow (\epsilon + \delta)$ | 1                                             | 342             | $5.93 \times 10^{-13}$ | 23                       | 100                     | 0.2                                    |
| 1    |                                            | 20                                            | 377             | $1.22 \times 10^{-12}$ | 11                       | 5                       | 2.2                                    |
| 2    | $(\epsilon + \delta) \rightarrow \delta$   | 1                                             | 400             | $5.37 \times 10^{-12}$ | 2.7                      | 90                      | 0.03                                   |
| 2    |                                            | 20                                            | 457             | $1.25 \times 10^{-11}$ | 1.1                      | 4                       | 0.27                                   |
| 3    | $(\delta + \alpha) \rightarrow \alpha$     | 1                                             | 710             | $1.65 \times 10^{-10}$ | 0.08                     | 200                     | $4 \times 10^{-4}$                     |
| 3    |                                            | 20                                            | 858             | $4.37 \times 10^{-10}$ | 0.03                     | 13                      | $2 \times 10^{-3}$                     |

constant at that temperature calculated from Eq. 8. The characteristic hydrogen diffusion time can be compared to an approximate characteristic hydrogen desorption time ( $\tau_{des}$ ) for a particular peak in the hydrogen desorption spectrum:

$$\tau_{des} = \Delta T / \beta \quad (10)$$

where  $\Delta T$  is the DTG peak width and  $\beta$  is the heating rate. Table 1 shows the characteristic diffusion and desorption times at each stage of decomposition at the fastest and slowest heating rate. This analysis neglects the possible role of a thin surface oxide layer. However, the effect is like to be insignificant due to the very low oxygen content ( $\sim 0.2$  wt. %) in the starting powder and lack of any measurable hafnia formation in the TGA curves until above  $\sim 700^\circ\text{C}$  and at heating rates  $< 10^\circ\text{C}.\text{min}^{-1}$ .

The table shows that for peak 1,  $\tau_{diff}$  and  $\tau_{des}$  are comparable, therefore it is possible that diffusion will play a role. For the faster heating rates and/or largest particles it is likely to be rate limiting. However, for peaks 2 and 3,  $\tau_{diff} \ll \tau_{des}$  which suggests that for these peaks diffusion is not rate limiting. The relatively symmetric shape of peak 2 suggests 1<sup>st</sup> order interface reaction limited kinetics, as proposed by Castro [24]. This suggests that what limits this reaction is the rate of hydrogen atoms migrating from the shrinking  $\epsilon$ -phase to the growing  $\delta$ -phase region. In the following section, the rate limiting steps for peak 3 are discussed.

#### 4.2. Rate equation for $\delta \rightarrow \alpha$ transformation

Peak 3 was shown in Fig. 7 to account for the  $\delta \rightarrow (\alpha + \delta)$  phase transition and thus results in  $\sim 80\%$  of the overall desorption. Identification of its mechanism is therefore of paramount importance. This task was challenging, due to the strong overlap of peaks 2 and 3. Therefore, a two-stage heating experiment was designed, where powders were first heated slowly to  $420^\circ\text{C}$  at  $1^\circ\text{C}.\text{min}^{-1}$  and cooled (this temperature was chosen, being significantly above the 2<sup>nd</sup> peak at  $400^\circ\text{C}$ ). The XRD for the powder at  $420^\circ\text{C}$  (Fig. 5b) shows that after this initial treatment, only the  $\delta$ -phase is present in the powder, (albeit with some  $\delta'$  formed on cooling). After this, a second heating was undertaken from 25 to  $850^\circ\text{C}$  at a rate of  $5^\circ\text{C}.\text{min}^{-1}$ . This intermediate heating rate minimises noise and oxidation in the measurement, which are more prevalent at low heating rates, while reducing peak broadening which is seen at higher heating rates.

Fig. 12 shows the rate of hydrogen loss for the second heating as a function of temperature. The peak is narrower than the corresponding peak in Fig. 5a due to the lack of overlap with peak 2. It shows an exponentially growing trend, followed by a sharp drop to a rate of zero

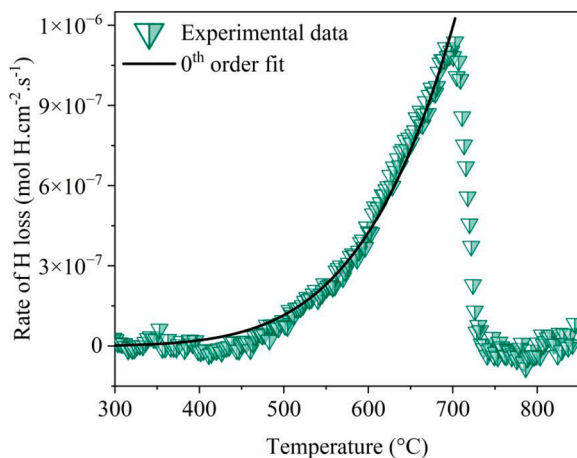


Fig. 12. Rate of H desorption from powder previously heated to  $420^\circ\text{C}$  and recycled at  $5^\circ\text{C}.\text{min}^{-1}$  from room temperature to  $850^\circ\text{C}$ . The data leading up to the peak has been fit with Eq. (11).

at  $\sim 700^\circ\text{C}$ , at which point all the hydrogen was desorbed.

As suggested by Castro and Gabis [23,24], an exponentially increasing peak followed by a sudden drop is evident of zeroth-order surface limited kinetics, where the rate is independent of hydrogen concentration and therefore entirely dependent on temperature through the surface desorption rate constant:

$$K = K_0 \cdot \exp\left(\frac{-E_{act}}{R.T}\right) \quad (11)$$

Where  $K_0$  is the pre-exponential factor ( $\text{s}^{-1}$ ) that depends on the surface area. By fitting this expression to the data in Fig. 12 in the range  $200$ – $700^\circ\text{C}$ , i.e. up to the peak temperature, we obtain an  $R^2$  value of 0.99, a  $K_0$  value of  $9.92 \times 10^{-3} \text{ mol H.cm}^{-2}.\text{s}^{-1}$ , and an activation energy of  $73 \pm 1 \text{ kJ.mol}^{-1}$ . This agrees well with the value extracted from the Kissinger analysis ( $86 \pm 9 \text{ kJ.mol}^{-1}$ ) giving confidence in the interpretation of surface limited kinetics.

It should be noted that these values do not agree with the calculated energy through DFT ( $148 \text{ kJ.mol}^{-1}$ ). This may be because the DFT does not account for the two-phase region ( $\alpha + \delta \rightarrow \alpha$ ) and instead calculates the desorption from a single phase. Future calculations should focus on comparing surface H-H recombination reactions on Hf-H phases as well as  $\text{H}_2$  desorption from the Hf surface. Finally, these activation energies can be compared with known reaction enthalpies. Luo et al. [42] showed via calorimetry of the Hf-deuteride system that the  $\alpha \rightarrow \delta$  hydrogenation reaction enthalpy is  $-70 \text{ kJ.mol}^{-1}$  which matches well with our experimental results from the Kissinger analysis ( $86 \pm 9 \text{ kJ.mol}^{-1}$ ) and the 0<sup>th</sup> order fit ( $73 \pm 1 \text{ kJ.mol}^{-1}$ ) for the  $\delta \rightarrow (\alpha + \delta)$  transition.

#### 4.3. Thermal desorption map

Based on the rate equation developed in section 4.2, we now propose a thermal desorption map, which serves as an engineering tool to inform device operation limits in a nuclear engineering scenario involving larger hydride part sizes. The tool can also guide powder consolidation strategies for hydride powders of a given size. To construct the map, we made the following assumptions: First, the starting composition of the hydride is assumed to be the maximum possible while still being fully  $\delta$ -phase at room temperature ( $\text{HfH}_{1.78}$  according to Fig. 1). Second, the pre-exponential factor  $K_0$  is directly proportional to the part's surface area (NB: this assumes that desorption is always surface limited). Third, the part is assumed perfectly spherical, for simplicity. Based on this

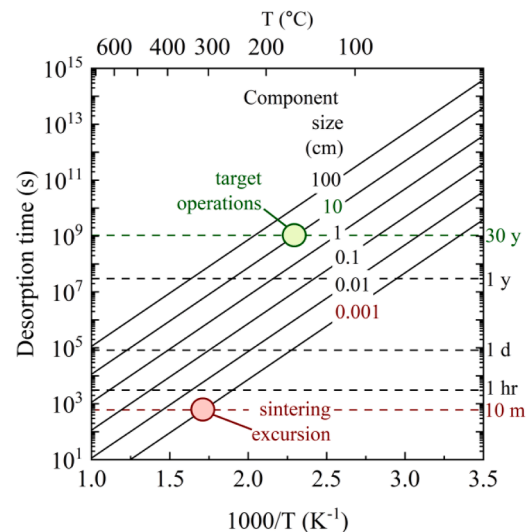


Fig. 13. A time-temperature desorption map for 10 % hydrogen desorption from  $\delta\text{-HfH}_{1.78}$ , as predicted by Eq. (11). Limits of reactor operation (30 years) are indicated by the green circle; limits of sintering excursion (10 min) by the red circle.

geometry, for a given part diameter and temperature, the time required to desorb 10% of the part's hydrogen can be calculated using Eq. 11. We consider a 10% hydrogen loss (equivalent to a  $\text{HfH}_{1.78} \rightarrow \text{HfH}_{1.6}$  transformation, i.e. towards the lower limit of the single  $\delta$ -phase region on Fig. 1) to be the maximum safe limit without any phase change or significant shape change. These desorption times are plotted in Fig. 13 as a function of temperature for various part diameters, in logarithmically increasing increments.

The thermal excursion for an anticipated device operation is shown in Fig. 13 as a green circle. Its position is determined by the intersection of the 30-year operational lifetime (dotted green line) and a part size on the order of 10 cm (solid green line). The intersection of this point and the x-axis corresponds to a maximum operating temperature of  $\sim 170^\circ\text{C}$ . Meanwhile for 1 year of operations the maximum temperature is  $\sim 250^\circ\text{C}$ . Engineering considerations such as cooling channels, coatings and periodic re-hydriding of the part would be required for the material to operate at higher temperatures.

The thermal excursion for a typical sintering run is presented as a red circle. Its position is determined by the intersection of the 10 min excursion (red dotted line) and a particle size of  $10\ \mu\text{m}$  ( $0.001\ \text{cm}$ ), with is slightly larger than the  $7.4\ \text{mm}$  particle size in this study (solid red line). The intersection of this point on the x-axis correspond to a maximum sintering temperature of typical sintering excursions are shown to be on the order of  $300^\circ\text{C}$ . For  $100\ \mu\text{m}$  particles the maximum sintering temperature is  $\sim 400^\circ\text{C}$ . These temperatures are well below those required to densify monolithic Hf-H [43]. Sintering in a hydrogen rich pressure, and/or entraining particles in a composite approach [8, 44] may therefore be required to sinter powders into fully dense parts.

#### 4.4. Comparison to other metal hydrides

The activation energies for other group IV metal hydride (Ti-H and Zr-H) powders have previously been evaluated via Kissinger analysis. For Ti-H activation energies for desorption of  $63\text{--}166\ \text{kJ}\cdot\text{mol}^{-1}$  are reported [45,46]. For the Zr-H system reported activation energies lie in the range  $114\text{--}188\ \text{kJ}\cdot\text{mol}^{-1}$  [46–48]. Table 2 shows a comparison of the mechanistic details compiled in this study of Hf-H with the analogous Zr-H system, for which the phase diagram is similar to Hf-H, albeit with a high temperature  $\beta$ -ZrH phase that is stable above  $550^\circ\text{C}$ .

For Zr-H the activation energies for desorption increase between in the 1<sup>st</sup> ( $\epsilon \rightarrow (\epsilon+\delta)$ ) and 2<sup>nd</sup> ( $(\epsilon+\delta) \rightarrow \delta$ ) desorption stages. The rate-determining step for each stage in Zr-H desorption was discussed to be limited by phase transformation by Ma et al. This aligns with our hypothesis for the  $(\epsilon+\delta) \rightarrow \delta$  stage but does not for the initial  $\epsilon \rightarrow (\epsilon+\delta)$  stage. It is likely that the discrepancy for the initial stage is due to the higher stability of  $\epsilon$ -ZrH<sub>2</sub> powder, which begins desorbing at  $\sim 480^\circ\text{C}$ , compared to  $\epsilon$ -HfH<sub>2</sub>, which begins at  $\sim 300^\circ\text{C}$ . This means that diffusion rates would be several orders of magnitude faster for ZrH<sub>2</sub> and therefore were likely not rate limiting. Indeed, Ma et al calculated the  $\tau_{\text{diff}}$  and  $\tau_{\text{des}}$  times using the same procedure used in Table 1, and showed that the latter was approximately 500 times greater, confirming the physical origin of the mechanistic discrepancy with this study.

Terrani and Hu provide a detailed investigation of desorption from bulk  $\delta$ -ZrH<sub>1.6</sub> finding 0<sup>th</sup> order kinetics in their data and relating this to

surface limited recombination of hydrogen being the rate limiting step. This directly supports our mechanistic understanding of the desorption through the  $\delta \rightarrow (\delta+\alpha)$  region for Hf-H which can also be well fit with 0<sup>th</sup> order kinetics. Terrani also discusses the close comparison of activation energy of hydrogen desorption to the enthalpy of formation of zirconium hydride of Zr-H, a point we discussed in Section 4.2.

Other reports of surface limited kinetics in hydrides are reported in the literature for Mg-H and U-H [53–55]. In the case of U-H, first principles calculations showed that out of 2 possible surface processes: H<sub>2</sub> formation and U-H-H surface recombination. The latter required much higher energy ( $2\text{--}36\ \text{kJ}\cdot\text{mol}^{-1}$  compared to  $115\text{--}96\ \text{kJ}\cdot\text{mol}^{-1}$  respectively [56,57]). This supports our interpretation of the surface combination being the rate limiting process for the  $\delta \rightarrow (\delta+\alpha)$  reaction.

To put the stability of Hf-H system into context, the H density in the material as a function of temperature is plotted with other nuclear relevant metal hydrides in Fig. 14. It should be noted that data for Y-H and Zr-H are taken from solid bulks, rather than powders, therefore the comparison may underestimate the relative stability of Hf-H. In the range  $0\text{--}300^\circ\text{C}$  the H densities are all similar. However, in the range  $300\text{--}500^\circ\text{C}$ , i.e. after the  $\text{YH}_3 \rightarrow \text{YH}_2$  transition, the H densities follows the trend  $\text{Zr} > \text{Hf} > \text{Y}$ . Above  $500^\circ\text{C}$ , i.e. after the  $\text{HfH}_2 \rightarrow \text{HfH}_{1.6}$  transition  $\text{Zr} > \text{Y} > \text{Hf}$  and then above  $900^\circ\text{C}$ , i.e. after the  $\text{ZrH}_{1.6} \rightarrow \text{Zr}$  transition the order is  $\text{Y} > \text{Zr} > \text{Hf}$  with Hf-H having fully desorbed.

The relatively poor stability of Hf-H compared to Y-H and Zr-H systems poses an engineering challenge for implementing the material in reactor operations. Given our analysis, which suggests that the  $\delta$ -phase desorption is limited by surface reaction, a surface coating or cladding system may prove to be effective. Our analysis suggests that it will be important to minimise any increase in apparent surface area resulting from interconnected porosity, which will otherwise increase the hydrogen desorption rate.

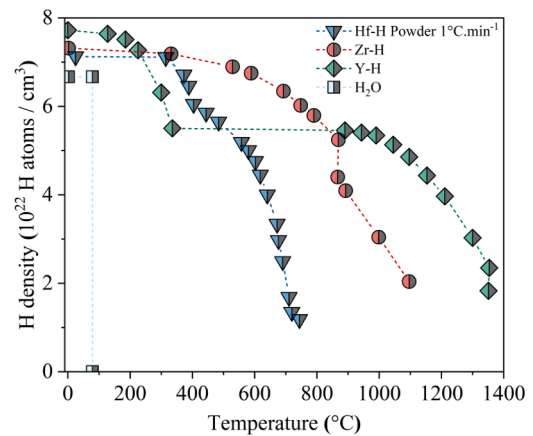


Fig. 14. Hydrogen density of neutron shielding/moderator materials plotted against temperature. Hf-H (this study), H<sub>2</sub>O, Zr-H and Y-H values adapted from [2].

Table 2

The reported activation energies and (in brackets) rate limiting mechanisms from the literature for Zr-H, compared to this study. In Refs. [44,45,48,49] the terminology *phase transformation limited* is used to describe the rate limiting mechanism, here we assume this is analogous to *interface limited*.

| Authors                | Method                      | Material                            | $\epsilon \rightarrow (\epsilon+\delta)$            | T (°C)  | $(\epsilon+\delta) \rightarrow \delta$              | T (°C)  | $\delta \rightarrow (\delta+\alpha)$                                                              | T (°C)  |
|------------------------|-----------------------------|-------------------------------------|-----------------------------------------------------|---------|-----------------------------------------------------|---------|---------------------------------------------------------------------------------------------------|---------|
| This study             | Dynamic TG-DTA              | $\epsilon$ -HfH <sub>2</sub> powder | 154–161 kJ·mol <sup>-1</sup><br>(diffusion limited) | 300–370 | 173–176 kJ·mol <sup>-1</sup><br>(interface limited) | 400–450 | 75–86 kJ·mol <sup>-1</sup><br>(surface limited)<br>–205 kJ·mol <sup>-1</sup><br>(surface limited) | 450–700 |
| Terrani and Hu [49,50] | Isothermal TDS              | $\delta$ -ZrH <sub>1.6</sub> bulks  | –                                                   | –       | –                                                   | –       | –                                                                                                 | 527     |
| Ma [47,48,51,52]       | Isothermal & dynamic TG-TDS | $\epsilon$ -ZrH <sub>2</sub> powder | 120 kJ·mol <sup>-1</sup><br>(interface limited)     | 477–577 | 147–167 kJ·mol <sup>-1</sup><br>(interface limited) | 600–700 | –                                                                                                 | –       |

## 5. Conclusions

The thermal stability and kinetics of hydrogen desorption of HfH<sub>2</sub> powder has been evaluated using dynamic thermogravimetry and X-ray diffraction. Three major peaks in the decomposition profile were observed. Interrupted XRD suggests that peak 1, which generally occurred at ~300–350°C, is related to the onset of decomposition of the hydrogen rich phase ( $\epsilon$ -HfH<sub>2</sub>) to form  $\delta$ -HfH<sub>1.6</sub>, i.e., the  $\epsilon \rightarrow \epsilon + \delta$  reaction. Peak 2 was related to the subsequent elimination of the  $\epsilon$ -HfH<sub>2</sub> phase, i.e., the  $\epsilon + \delta \rightarrow \delta$  reaction. Finally, peak 3 was related to the conversion of  $\delta$ -HfH<sub>1.6</sub> to metallic  $\alpha$ -Hf, i.e., the  $\delta \rightarrow \alpha$  reaction.

For the  $\epsilon \rightarrow \epsilon + \delta$  reaction (peak 1), diffusion of hydrogen out of the shrinking  $\epsilon$  phase is of the same order of magnitude as the characteristic desorption time and could therefore be the rate limiting step. The result differs from studies on  $\epsilon$ -ZrH<sub>2</sub> desorption, but may explained by decomposition in the HfH<sub>2</sub> system occurring at a temperature ~200°C lower. The activation energy for the process was calculated using the Kissinger method to be  $161 \pm 29$  kJ.mol<sup>-1</sup>, which was in good agreement with DFT simulation of 154 kJ.mol<sup>-1</sup>. HTXRD measurements show that as hydrogen was desorbed from the shrinking  $\epsilon$ -HfH<sub>2-x</sub> phase its c-parameter expanded whereas the a-parameter contracted.

For the  $\epsilon + \delta \rightarrow \delta$  reaction (peak 2), it is likely that atomic jumps of hydrogen across the interface between the shrinking  $\epsilon$  and the growing  $\delta$  are rate limiting. This conclusion is supported by the combined symmetric peak shape and the fast characteristic diffusion distances at the peak temperature, and is in agreement with studies on the Zr-H system. The activation energy was calculated to be  $173 \pm 8$  kJ.mol<sup>-1</sup>, again in close agreement with DFT of 176 kJ.mol<sup>-1</sup>.

For the  $\delta \rightarrow \alpha$  reaction (peak 3), the surface recombination of hydrogen atoms to form gaseous H<sub>2</sub> is found to be rate limiting, owing to it being well fit with a zeroth-order kinetic law, again in agreement with the Zr-H system. The activation energy calculated using the kinetic law fit showed excellent agreement with the Kissinger analysis (73 and 86 kJ.mol<sup>-1</sup> respectively).

The thermal desorption map developed suggests that, at least for a shield on the order 10cm thick and a required operating lifetime of 30 years, the maximum service temperature may be approximately 200°C. Comparing the thermal stability of Hf-H with other candidate nuclear materials Zr-H and Y-H suggests efforts to improve stability should be explored. Future work may consider surface claddings and/or high density (+90%) processing methods to minimise the exposed surface area. More detailed characterisation of the desorption in such materials may be beneficial, including more direct methods such as thermal desorption spectrometry.

## CRedit authorship contribution statement

**J.P. Pollard:** Conceptualization, Investigation, Writing – original draft, Visualization. **A. Dumain:** Investigation, Writing – review & editing. **B. Stratton:** Investigation, Writing – review & editing. **S. Irukuvarghula:** Writing – review & editing. **J. Astbury:** Conceptualization, Resources, Supervision, Funding acquisition. **S. Middleburgh:** Conceptualization, Resources, Writing – review & editing, Supervision, Funding acquisition. **F. Giuliani:** Conceptualization, Resources, Writing – review & editing, Supervision, Funding acquisition. **S. Humphry-Baker:** Conceptualization, Resources, Writing – review & editing, Supervision, Funding acquisition.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.jnucmat.2024.155499](https://doi.org/10.1016/j.jnucmat.2024.155499).

## Data availability

Data will be made available on request.

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