



# Non-isothermal and isothermal hydrogen desorption kinetics of zirconium hydride



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## HIGHLIGHTS

- The mechanism of  $ZrH_2$  decomposition was studied by simultaneous TG-TDS technique.
- Phase transformation sequences under different heat treatments were obtained.
- The held temperature would affect the isothermal phase transformation sequences.
- The  $\gamma ZrH$  phase can be formed by quenching from high temperature.

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## ABSTRACT

Thermal desorption behaviors of zirconium hydride powder under non-isothermal and isothermal heat treatment conditions were studied using simultaneous TG-TDS. The phase transformation sequences were established by correlating the observed peaks of  $H_2$  release and mass loss. The origins of the peaks or shoulders in the TDS spectra were described as the equilibrium hydrogen pressures of a number of consecutive phase regions that decomposition reaction passed through. Effect of held temperature on the isothermal desorption behavior was taken into consideration, which was shown to be essential for the phase transformation sequence during  $ZrH_2$  decomposition. The zirconium monohydride  $\gamma ZrH$  was observed at ambient conditions, which has been supposed to be metastable for a long time.

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## 1. Introduction

Zirconium hydride is widely employed in nuclear technology. It is potentially one of the most ideal moderators because of its high content of hydrogen, high neutron scattering cross-section, low neutron absorption cross-section and negative temperature coefficient of reactivity [1]. In other instances, it is purposefully used for the uranium–zirconium hydride fuel, which is a two-phase mixture consisting of zirconium hydride matrix and small uranium particles, and has been utilized in numerous occasions such as Space Nuclear Auxiliary Power (SNAP) program and Training, Research, Isotopes, General Atomic (TRIGA) research reactors [2,3]. However, hydrogen would escape from zirconium hydride at the reactor working temperature (e.g. peak temperature of 1123 K for SNAP reactor and 823 K for light water reactor (LWR) [2]). This may

affect the stability and integrity of zirconium hydride, which is the major performance constraint for these reactors. Although many studies on the thermodynamic, thermal, mechanical and electrical properties of zirconium hydride have been reported [4–9], limited information is available on hydrogen desorption kinetic process [10–13]. Therefore, it is required to investigate the hydrogen desorption kinetics of zirconium hydride under different heat treatments, which is important for understanding the final state of the hydride, such as the amount of hydrogen remaining after thermal processing.

Thermal desorption spectroscopy (TDS), a technique initially developed for the study of the kinetics of gas–solid surface interactions, has been commonly used to identify the rate-controlling step of  $H_2$  evolution and obtain the kinetic parameters for many metal hydrides [14–17]. In most cases, the information obtained from TDS spectra of metal hydrides is difficult to interpret because it should take into account several processes, e.g. surface processes, bulk processes and different thermodynamic phases [18]. On the

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other hand, the decomposition processes of metal hydrides can be studied by means of thermal analysis techniques such as thermogravimetry (TG) and differential scanning calorimetry (DSC). The simultaneous use of both thermal analysis and gas analysis techniques (TG-TDS, DSC-TDS, etc) provides the possibility of obtaining complete information on the thermodynamics and kinetic properties of metal hydrides [19–23]. For example, Fernández [20] employed DSC–TDS technique to study the decomposition of  $\text{TiH}_2$  powders and found a good correlation between hydrogen desorption and heat absorption. Matijasevic-Lux [24] and Jiménez [25] used TG-TDS to investigate the decomposition characteristics of  $\text{TiH}_2$  powders by prior thermal and oxidizing pre-treatments. Among these simultaneous techniques, TG-TDS is an effective tool to examine the decomposition of metal hydride since it has several advantages. Firstly, structural transformations can easily be distinguished for the reason that the information of the conversion of the solid state decomposition and the hydrogen gas evolution are obtained in the same temperature interval. This would allow us to attribute the peaks of TDS spectra to the corresponding phase transformation steps. Secondly, experimental errors due to changes in sample characteristics are avoided as the same sample is used [20].

In our previous work [26], we have investigated the thermal desorption kinetics of zirconium hydride powder at a series of heating rates using TG-TDS methods. In this study, we perform additional TG-DSC studies and compare them with TG-TDS results, aiming at identifying the sequences of phase transformation and the origins of TDS spectra peaks. Furthermore, we present the isothermal studies of  $\text{ZrH}_2$  desorption held at three different temperatures for long periods of nearly 1000 min.

## 2. Experimental

The as-received commercial  $\text{ZrH}_2$  powder (99% pure), with particle size ranging from less than 1  $\mu\text{m}$ –30  $\mu\text{m}$ , was characterized using scanning electron microscope (ProX, Phenom, Netherlands) and laser particle size analyzer (1064L, CILAS, France). The decomposition of  $\text{ZrH}_2$  was studied by TG-TDS (IGA-003, Hiden, UK) and TG-DSC (STA 449 F3 Jupiter, Netzsch, Germany) methods. In IGA-003, an ultra-sensitive microbalance of resolution 0.2  $\mu\text{g}$  is mounted in the thermostated heatsink with high precision temperature control. The sample was loaded in a quartz sample container and suspended from the hangdown quartz hook connected to the microbalance. Before measurements, the quartz reactor tube was vacuumed up to  $10^{-5}$  Pa and then pure argon gas ( $\geq 99.99\%$ ) was used as carrier gas with a flow rate of 50 ml/min. The emitted  $\text{H}_2$  was measured using quadrupole mass spectrometer (QMS) connected to IGA-003 through a thin capillary tube that can be heated to 473 K to avoid vapor condensation. In non-isothermal experiments, the samples were heated up to 1253 K with the linear temperature ramps of 2, 5, 10 and 20 K/min, respectively. The isothermal TG-TDS analyses were kept at 773, 873 and 973 K for nearly 1000 min, respectively, with the prior heating rate of 20 K/min.

The TG-DSC experiments were performed in aluminum oxide pans with pierced lid at the linear heating rates of 2, 5, 10 and 20 K/min, respectively. The apparatus was vacuumized by roughing pump and refilled with pure argon gas ( $\geq 99.99\%$ ) twice before the measurements. The samples were heated up to 1573 K under flowing argon atmosphere kept at a rate of 50 ml/min. In all the TG-TDS and TG-DSC measurements a constant amount of 100 mg of as-received  $\text{ZrH}_2$  powder was used.

The phase structures were identified by XRD (Rigaku D/Max-2400) using  $\text{Cu-K}\alpha$  radiation, at a scanning rate of  $4^\circ/\text{min}$  using a generator voltage of 40 kV and a current of 150 mA. All the XRD

measurements were carried out at room temperature and the phase composition was determined on base of JCPDS files provided by the International Center for Diffraction Data.

## 3. Results and discussion

### 3.1. Non-isothermal desorption kinetics

Fig. 1 shows particle size distribution analysis and the SEM image of the as-received  $\text{ZrH}_2$  powder. The mean size of the powder is about 12  $\mu\text{m}$ . Morphology is represented by irregular polyhedrons with sharp edges and cleavage planes. The simultaneously obtained TG and TDS results of the total  $\text{ZrH}_2$  decomposition for various heating rates are shown in Fig. 2(a) and (b), which have been published elsewhere [26]. The H/Zr atom ratios were calculated from the mass losses obtained from TG measurements. It can be seen that prominent  $\text{H}_2$  release accompanied by mass loss starts at approximately 650 K, independent of heating rate. The TDS spectrum consists of one main peak (Peak IV), three low-temperature (Peak I, II and III) and one high-temperature (Peak V) shoulders. With the increase of heating rate, all the five peaks shift to high temperature. In order to check the TDS results, TG-DSC experiments were carried out under the similar conditions, including sample mass, heating rate and flow rate. The DSC results at different heating rates are shown in Fig. 2(c). TG results obtained simultaneously in the TG-DSC measurements are not shown here for the reason that they are in good agreement with the TG curves in Fig. 2(a). Similar to TDS spectra, the DSC curves also show the structure of multi-peak.

Fig. 3 shows the XRD spectra of as-received  $\text{ZrH}_2$  powder and  $\text{ZrH}_2$  powder after TG-TDS measurement. The original zirconium hydride containing nearly 2H/Zr was identified as  $\epsilon$  phase (space group  $I4/mmm$ ) with lattice constants  $a = 0.499$  nm,  $c = 0.445$  nm. The  $\epsilon$  phase exists as a single phase at hydrogen concentrations roughly above  $\text{ZrH}_{1.7}$  at room temperature [27]. It has a distorted-fluorite fct structure,  $c/a < 1$ , in which hydrogen occupy tetrahedral positions, and the lattice parameters vary with composition [27]. After TG-TDS measurement, the sample has the pure structure of  $\alpha\text{Zr}$  ( $a = 0.324$  nm,  $c = 0.517$  nm), indicating that the decomposition has been completely finished.

Identifying the rate-limiting step is helpful for understanding the desorption process. It is usually assumed for simplicity that one of the elementary reaction steps is considerably slower than other steps, and therefore the kinetics of this particular step controls the overall reaction rate (there is a rate-limiting step). For metal hydride, there are several potential rate-limiting steps, including bulk diffusion, phase transformation, bulk to surface transfer and surface recombination [28]. A simple criterion was used to determine if diffusion can be a rate-limiting step [14,29,30].

Assuming the diffusion concept, the value of  $\tau_{dif}$ , which is defined as the diffusion time necessary to traverse the particle radius, is estimated from the random-walk expression  $\tau_{dif} = d^2/D_{dif}$ , where  $d$  is the average particle radius (6  $\mu\text{m}$ ), and  $D_{dif}$  the diffusion coefficient of hydrogen atoms for a temperature at the TDS curve peak maximum ( $T_p$ ). Given that the heating rate is 20 K/min and the corresponding  $T_p$  is 1094 K, the  $D_{dif}$  for hydrogen diffusivity in various zirconium hydrides is on the order of  $10^{-6}$   $\text{cm}^2/\text{s}$  [31–33]. Then the value of  $\tau_{dif}$  can be estimated as 0.36 s. The characteristic desorption time during the thermal desorption experiment,  $\tau_{des}$ , is determined from the simple expression  $\tau_{des} = \Delta T/\beta$ , where  $\Delta T$  is the width of the desorption peak and  $\beta$  the heating rate. Taking a value of  $\beta = 20$  K/min and  $\Delta T = 250$  K as measured, one can estimate the  $\tau_{des}$  to be 750 s. The value is more than 2000 times larger than the diffusion time  $\tau_{dif}$ , and then it is safe to conclude that diffusion is not the rate-limiting step [14,29,30]. In other words, hydrogen

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