



# Decomposition kinetics study of zirconium hydride by interrupted thermal desorption spectroscopy



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## ABSTRACT

Thermal desorption kinetics of zirconium hydride powder were studied using thermogravimetry and simultaneous thermal desorption spectroscopy. The activation energies for observed desorption peaks were estimated according to Kissinger relation. The intermediate phase composition was studied using X-ray diffraction by rapid cooling on different stages of heating. The origins of the peaks were described as the equilibrium hydrogen pressure of a number of consecutive phase regions that decomposition reaction passed through. The zirconium monohydride  $\gamma\text{ZrH}$  was observed for extended periods of time 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 (e.g. as the moderators [1–4] and fuel [5–7] in reactors). However, hydrogen would lose from zirconium hydride at the reactor working temperature (e.g. peak temperature of 1123 K for the SNAP reactor and 823 K at the LWR [5]). This may affect the stability and integrity of hydride fuel, which is the major performance constraint for these reactors. Although many studies on the thermal, mechanical and electrical properties of zirconium hydride have been reported [8–11], limited information is available on hydrogen desorption kinetic process. It is required to understand the hydrogen desorption kinetics of zirconium hydride, 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) is commonly used to identify the rate-controlling step of  $\text{H}_2$  evolution and obtain the kinetic parameters for many metal hydrides [12–15]. Interrupted TDS, which means a step-by-step heating in thermal desorption regime interrupted by fast sample cooling, is especially useful to test intermediate phase composition and has been applied to study the decomposition kinetics of  $\text{TiH}_2$  by Borchers et al. [16].

In this work, decomposition kinetics of zirconium hydride powder were studied by conventional TDS and interrupted TDS in detail, with the goal of obtaining desorption kinetic parameters and identifying the origins of desorption peaks, respectively. Based on the combined analysis of interrupted TDS and X-ray diffraction

(XRD), the observed desorption peaks can be attributed to different phase transforming steps. Furthermore, the zirconium monohydride  $\gamma\text{ZrH}$  was observed once again for extended periods of time at ambient conditions, which has been supposed to be metastable for a long time [17 and references therein].

## 2. Experimental

Commercial  $\text{ZrH}_2$  powder (99% pure, 400 mesh) was used in this study. The decomposition of  $\text{ZrH}_2$  was studied by thermogravimetry and simultaneous thermal desorption spectroscopy (TG-TDS; IGA-003, Hiden, UK). The samples with the weight of nearly 100 mg were heated with a linear temperature ramp of 2, 5, 10, 12, 15 and 20 K/min up to 1253 K, respectively. The desorption hydrogen gas was measured using quadrupole mass spectrometer (QMS) under pure Ar gas ( $\geq 99.99\%$ ) flow conditions with a flow rate of 50 ml/min. Interrupted TDS experiments were carried out with a heating rate of 20 K/min by heating the samples to the chosen temperature, namely 795, 890, 1013 and 1109 K, and then cooling to room temperature at a rate of rough 40 K/min. 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

Fig. 1 shows the TG and TDS results of the total  $\text{ZrH}_2$  decomposition for various heating rate. The H/Zr atom ratio was calculated from the weight loss and the signal of  $\text{H}_2$  evolution rate has been normalized by sample weight. It can be seen that the TDS spectrum consists of one main peak (Peak IV) and 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

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temperature. The activation energy for each peak was determined according to Kissinger relation [18], which is presented in inset of Fig. 1(b). The values of activation energies derived from this plot are 120, 147, 167, 188 and 114 kJ/mol for Peak I, II, III, IV and V, respectively. The magnitude is coherent with the value of 160 kJ/mol for the enthalpy of formation of zirconium hydride through calorimetric experiments [19] and the value of 205 kJ/mol for the activation energy of hydrogen desorption from zirconium hydride through thermogravimetric analysis [7].

Fig. 2 shows a comparison of TDS spectra of the fresh  $ZrH_2$  powder and  $ZrH_2$  powder heated up to different temperature and then cooled to room temperature. It can be seen that the peaks disappear in turn from Peak I to Peak IV when the sample were quenched from 795 to 1109 K, while the peak positions of the residual peaks do not change for all the samples.

To establish a correspondence between the TDS spectra and structural evolution during decomposition the phase compositions of samples were determined by XRD after heated up to the chosen temperature and then cooled to room temperature, which are marked in Fig. 3. Table 1 summarizes corresponding TG-TDS and XRD data.

The original zirconium hydride containing nearly 2 H/Ti 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  $ZrH_{1.7}$  at room temperature [17]. It has a distorted-fluorite fct structure,  $c/a < 1$ , and the lattice parameters vary with composition [17]. After TDS was interrupted at 795 K, the sample still contains 1.83 H/Zr and has a structure of  $\epsilon ZrH_{1.801}$ . The lattice constants  $a$  decreases to 0.495 nm while  $c$  increases to 0.451 nm. After TDS was interrupted at 890 K, the sample contains 1.67 H/Zr and the structure mostly transfers to  $\delta ZrH_{1.66}$  ( $a = 0.478$  nm) phase. The  $\delta$  hydride has a fcc structure,  $CaF_2$ -type, in which hydrogen occupy tetrahedral positions. A weak peak observed at  $2\theta = 36.2^\circ$  was identified as the residual  $\epsilon ZrH_{1.801}$ , which was probably caused by the temperature difference inside the powder in the experiments.

After TDS was interrupted at 1013 K, the sample contains 1.35 H/Zr. The following three phases were detected:  $\delta ZrH_{1.66}$  ( $a = 0.478$  nm),  $\gamma ZrH$  ( $a = 0.460$  nm,  $c = 0.496$  nm) and  $\alpha Zr$  ( $a = 0.326$  nm,  $c = 0.518$  nm). The phase  $\gamma ZrH$  has a fct structure like the  $\epsilon$  phase from which it differs by having a lattice parameter ratio  $c/a$  greater than unity [17]. The H atoms occupy half of the tetrahedral sites in an ordered fashion, leading to a composition of H/Zr = 1. In early works,  $\gamma ZrH$  is supposed to be metastable, although it has been found under certain conditions (e.g., in the  $\alpha + \delta$  phase field, at temperatures below 528 K) from experimental results [17]. Many questions about  $\gamma$  phase still remain unanswered such as the exact composition ranges in which it

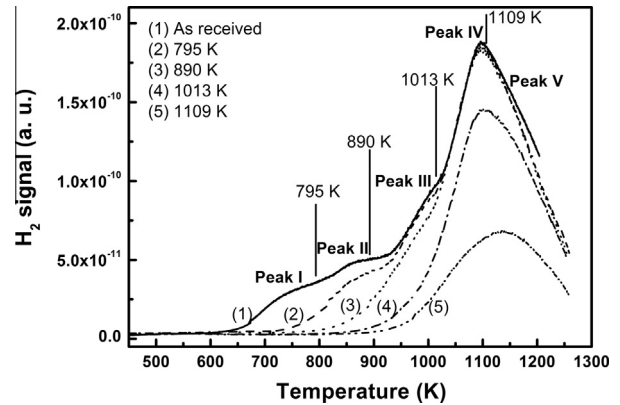


Fig. 2. TDS spectra of as received  $ZrH_2$  and  $ZrH_2$  heated up to different temperature and then cooled to room temperature.

exists, the conditions and mechanism of its precipitation, even its metastability and the possibility that it may be an equilibrium phase [17]. Since the XRD experiments were carried out more than 72 h after the heat treatment of the sample in our work, we can confirm that  $\gamma ZrH$  can exist for extended periods of time at ambient conditions, formed by quench from high temperature (e.g. 1013 K). After TDS was interrupted at 1109 K, the sample contains 0.63 H/Zr and still has the three phases:  $\delta ZrH_{1.66}$  ( $a = 0.478$  nm),  $\gamma ZrH$  ( $a = 0.461$  nm,  $c = 0.495$  nm) and  $\alpha Zr$  ( $a = 0.325$  nm,  $c = 0.517$  nm). Compared with the XRD pattern of sample quenched from 1013 K, it can be seen from the change of peak intensity that the amounts of  $\delta ZrH_{1.66}$  and  $\gamma ZrH$  reduce and that of  $\alpha Zr$  augments. The sample contains 0.03 H/Zr after decomposition was completely finished at 1253 K, with the pure structure of  $\alpha Zr$  ( $a = 0.324$  nm,  $c = 0.517$  nm).

The phase diagram of the Zr–H system [20,21] is shown in Fig. 4. ( $\gamma$ ) is put into brackets because the  $\gamma$  phase was supposed to be metastable in early works as discussed above. The initial position,  $\epsilon ZrH_2$ , is located at the bottom right corner. The solid line with upward arrows denotes the changing trend of temperature/hydrogen content obtained from the TG experiment at a heating rate of 20 K/min, which is extended with dash line toward high temperature because the experimental data was not obtained above 1200 K. The stars show the temperature points from which the heating was interrupted and the dash lines with downward arrows point to the corresponding H/Zr ratio in the sample. The phase transformation sequence for  $ZrH_2$  decomposition under heating linearly to 1253 K conditions can be schematized as follows:

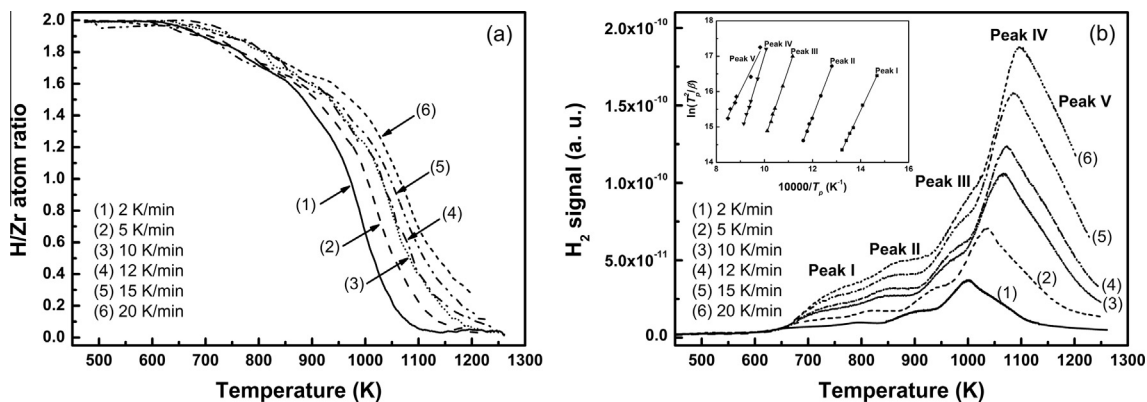


Fig. 1. TG (a) and TDS (b) spectra of as received  $ZrH_2$  at different heating rate. Inset of (b) shows the Kissinger plot for different desorption peaks.

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