



# Oxidation behaviour of zirconium hydride and its influence on the thermal desorption kinetics

Mingwang Ma, Lei Wang, Yuan Wang, Wei Xiang, Binghua Tang, Ping Lyu, Xiaohua Tan\*

Institute of Electronic Engineering, China Academy of Engineering Physics, Mianyang 621999, China

## ARTICLE INFO

### Keywords:

Zirconium hydride  
Thermal desorption spectroscopy  
XPS  
Oxidation kinetics  
Diffusion coefficient

## ABSTRACT

The oxidation kinetics of zirconium hydride powder in air was studied over the temperature range of 100–300 °C. The oxidation kinetic parameters were obtained and a controlling mechanism was proposed. The XPS depth profile analysis was consistent with a layered structure of the oxide film. The evolution of oxygen concentration profile allowed to estimate the diffusion coefficient of oxygen in zirconium oxide. Thermal desorption behaviours of pre-oxidized ZrH<sub>2</sub> were studied using simultaneous thermogravimetry and thermal desorption spectroscopy (TG-TDS). The phase transformation sequence during dehydrogenation process of pre-oxidized ZrH<sub>2</sub> was established and a corresponding shrinking core model was proposed.

## 1. Introduction

Zirconium hydride (ZrH<sub>2</sub>) 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]. However, hydrogen evolves from the zirconium hydride at the reactor working temperature, which is one of the main limiting factors of the stability and integrity of zirconium hydride [2]. Forming an oxide layer onto the surface of ZrH<sub>2</sub> to serve as a hydrogen permeation barrier is identified as the most promising route to resist hydrogen desorption from the hydride [3–5]. Understanding the effect of oxide layer on hydrogen desorption kinetics as well as the oxidation behaviour of ZrH<sub>2</sub> is of great significance to evaluate the performance of ZrH<sub>2</sub> in nuclear technology, as well as to develop new route to improve the properties of ZrH<sub>2</sub>. Many studies on the behaviour of hydrogen in zirconium alloys and how the oxidation is affected by the hydride phase have been reported [6–9]. However, the comprehension of the mechanism of the interactions in the Zr-H-O system is a major unsolved issue [10,11]. There is evidence that the hydrogen enrichment can promote a segregation of oxygen to the surface [12]. Conversely, the increase in oxygen concentration can cause gradual substitution of the metallic bonds by covalent and ionic bonds [11]. Nevertheless, limited information is available on hydrogen desorption kinetics of ZrH<sub>2</sub> with an oxide layer on its surface [13,14].

The oxidation kinetics of Zr alloys has been extensively studied under several oxidation conditions in order to elucidate the mechanism of oxide growth and breakdown [7–9,15,16]. It has been revealed that the microstructures and properties of the grown oxide films depend on

the exact alloy composition and on the environment in which oxidation occurs [17]. The thermal oxidation of Zr alloys is generally described by an initial cubic or parabolic pre-transition stage followed by a quasi-linear variation law [18,19]. The effect of the precipitated hydrides or dissolved hydrogen on the oxidation behaviour of Zr alloys has been investigated in previous studies [20,21]. A higher oxidation rate of zirconium hydride phase compared with Zr alloys and a notable change in the oxide structure are often observed and the mechanism is still in debate [6,20]. It is suggested that the enhanced oxidation rate is due to the precipitation of massive hydrides at the metal/oxide interface [20]. The hydride precipitated in the  $\alpha$ -Zr crystalline lattice induces a loss of coherency with the zirconia lattice, and thereby a less protective oxide barrier at the interface. The oxidizing species in this layer would diffuse more easily through the scale to reach the metal/oxide interface, leading to an accelerated oxidation [20]. While Oskarsson et al. [22] argued that the oxidation of zirconium hydride resembles the oxidation of Zr metal, and the accelerated oxidation for the pre-hydrided Zr is due to a combination effect of hydride precipitation and interfacial roughness.

Many studies have been performed on purpose to evaluate the effect of oxide layer on the desorption behaviour of metal hydrides [23]. For example, TiH<sub>2</sub> powders are usually pre-heated in air to form an oxide layer on the surface of the particles. The oxide layer acts as an effective diffusion barrier for hydrogen evolution, thereby shifting the onset and peak temperatures of hydrogen thermal desorption spectrum to higher temperature [24]. It is suggested that the TiO<sub>2</sub> rutile shell controls the outgassing from the pre-oxidized TiH<sub>2</sub> powder [25]. This effect is already known and has been exploited to control hydrogen evolution

\* Corresponding author.

E-mail address: [caepiee@163.com](mailto:caepiee@163.com) (X. Tan).

<https://doi.org/10.1016/j.corsci.2018.02.019>

Received 3 November 2017; Received in revised form 8 February 2018; Accepted 16 February 2018  
0010-938X/ © 2018 Elsevier Ltd. All rights reserved.

from  $\text{TiH}_2$  in metal foam manufacture [26–29]. The effect of oxide layer on the dehydrogenation process has also been mentioned for  $\text{ZrH}_2$ . Wongsawaeng et al. [30] found that the release rate of zirconium hydride for the case of the oxidized surface condition is much slower than the clean surface condition due to the presence of the oxide layer. Chen et al. [13] reported that the hydrogen desorption is restricted effectively if zirconium hydride is exposed to an oxygen containing atmosphere. It was suggested that the O–H bond in the oxide layer is beneficial to fix hydrogen atoms and prevent hydrogen diffusion [13,31]. Theoretical analysis has also indicated that the oxide layer withholds the effective hydrogen diffusion and decreases the hydrogen flux at the surface [32]. However, no widely accepted mechanism exists that describes how hydrogen penetrates the passive oxide layer that are formed on Zr alloys or  $\text{ZrH}_2$  [33].

In this work, the kinetics of hydrogen desorption from  $\text{ZrH}_2$  with different oxidation levels was explored. The oxidation experiments were conducted in flowing air at atmospheric pressure by thermogravimetry (TG) method. It was thought that a separate oxidation of metal and hydrogen release took place when the hydride was heated to the higher temperature [34,35]. To avoid hydrogen loss, the oxidation temperatures were selected in the range of 100–300 °C in this study, since hydrogen evolved from the oxide on Zircaloy slowly already at 300 °C and at about 500 °C hydrogen was quickly released from the oxide scale by cracking O–H bonds [31,36]. The selected temperature range also matched the operation environment for zirconium used as fuel rod cladding [37]. The decomposition of as-received and pre-oxidized samples was characterized by simultaneous thermogravimetry and thermal desorption spectroscopy (TG-TDS) analysis, which has been frequently used to identify the rate-controlling step of  $\text{H}_2$  evolution and obtain the kinetic parameters for many metal hydrides [38–40].

## 2. Experimental

### 2.1. Materials

Commercial  $\text{ZrH}_2$  powder (99% pure) was used in this study and characterized by scanning electron microscope (ProX, Phenom, Netherlands) for its morphology, and energy dispersive spectroscopy (EDS) for its element content. As shown in Fig. 1(a), the morphology is represented by irregular polyhedrons with sharp edges and cleavage planes. Fig. 1(b) presents the chemical composition of the powder by EDS, which indicates that zirconium is the predominant element at the surface and some impurities are revealed due to surface oxidation and contamination. The particle size distribution of the as-received powder was characterized by a laser particle size analyser (1064L, CILAS, France), which shows that the mean size of the powder is approximately 12  $\mu\text{m}$  (Fig. 2).

### 2.2. Oxidation tests

The isothermal oxidation was performed on a simultaneous thermal analysis instrument (STA 449 F3 Jupiter, Netzsch, Germany). As-received  $\text{ZrH}_2$  powders with the weight of approximately 150 mg were heated to the desired temperatures (100, 200 and 300 °C) at a linear temperature ramp of 20 °C/min in flowing argon ( $\geq 99.999\%$ , 50 ml/min). When the desired temperatures were reached, the gas was switched from argon to air with a flow rate of 50 ml/min. The oxidation tests at each temperature were repeated twice, which were named as Series 1 and Series 2, respectively. All the experiments were performed in aluminum oxide pans with pierced lid.

### 2.3. Characterization of samples

After oxidation tests, the pre-oxidized samples (Series 1) were characterized by means of X-ray diffraction (XRD) and X-ray

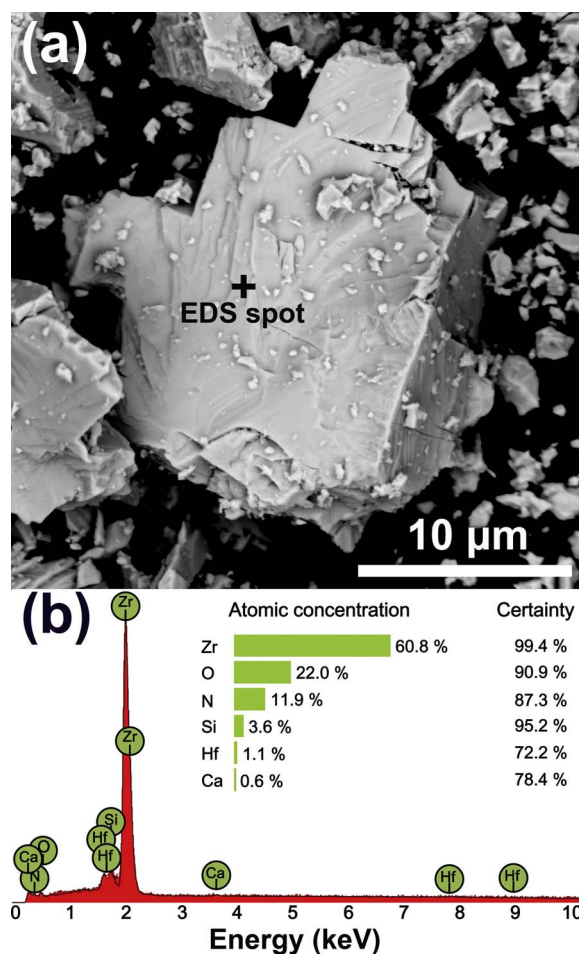


Fig. 1. SEM image of as-received  $\text{ZrH}_2$  powder (a) and its typical EDS spectrum (b).

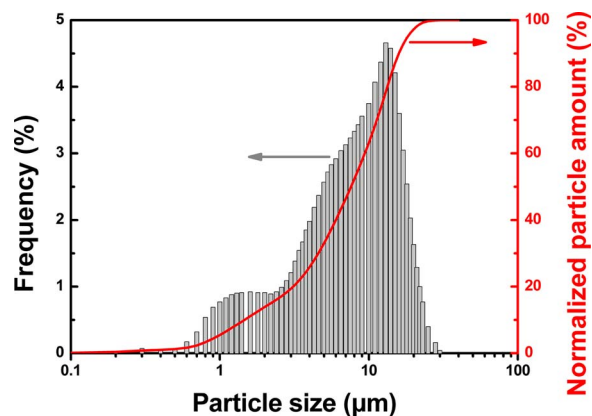


Fig. 2. Particle size distribution of as-received  $\text{ZrH}_2$  powders. The histogram indicates the amount of the particle at the size and read from left vertical axis. The line indicates the total amount of the particle up to the size and read from right vertical axis.

photoelectron spectroscopy (XPS) at room temperature. The phase structures were identified by XRD (Rigaku D/Max-2400) using  $\text{Cu-K}\alpha$  radiation, at a scanning rate of 4°/min with a generator voltage of 40 kV and current of 150 mA. The phase compositions were determined on the basis of JCPDS files provided by the International Center for Diffraction Data. Quantitative phase analysis was performed using the Rietveld refinement method [41]. The experimental patterns were fitted with a linear combination of the theoretical patterns and of the background using optimized values of lattice parameters and parameters of broadening the diffraction maxima of phases.

Download English Version:

<https://daneshyari.com/en/article/7893719>

Download Persian Version:

<https://daneshyari.com/article/7893719>

[Daneshyari.com](https://daneshyari.com)