

Hydrogen desorption behaviors of zirconium hydride in oxygen containing atmosphere

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Abstract: Hydrogen desorption behaviors of zirconium hydride at temperature range of 100–900 °C in mixture gases of helium and oxygen was studied by gas phase analysis(GPA). Meanwhile, the morphologies of the oxide scale formed on the surface of zirconium hydride were analyzed by scanning electron microscopy(SEM). The hydrogen desorption is retarded effectively when zirconium hydride is exposed to an oxygen containing atmosphere. Hydrogen desorption in mixed gas of helium and oxygen starts at 525 °C and reaches maximum at 660 °C and ends eventually at 800 °C. No hydrogen desorption is found at the temperature range from 800 °C to 900 °C. An oxide scale with approximately 20 μm in thickness formed on the surface of zirconium hydride acts as an effective diffusion barrier.

Key words: zirconium hydride; gas phase analysis(GPA); hydrogen desorption; oxide scale

1 Introduction

Zirconium and its alloys have been found their main applications in nuclear engineering for its excellent corrosion resistance, good mechanical properties and low neutron absorption cross section[1–2]. Zirconium hydride with high hydrogen content ($H/Zr > 1.5$) is one of the most ideal moderators used in space nuclear reactors[3–4]. The nuclear, physical and thermal properties, which are important for safe use of zirconium hydride in nuclear reactors, had been widely studied during the last few decades[5–6]. However, the problem of hydrogen loss of zirconium hydride at the range of working temperatures has not been solved satisfactorily, which limited the application of zirconium hydride in nuclear reactors.

Forming an oxide scale on the surface of zirconium hydride served as the hydrogen permeation barrier is identified as the most promising rout to reduce hydrogen loss. The researches of zirconium hydride oxidized in carbon dioxide to obtain the hydrogen permeation barrier have been reported recently[7]. Limited information is available on hydrogen desorption behaviors of zirconium hydride in oxygen containing atmospheres. Considering that zirconium hydride is usually working in oxidizing

circumstance[8], it is important to understand the hydrogen desorption behaviors of zirconium hydride in oxidizing atmosphere.

In the present work, the hydrogen desorption behaviors of zirconium hydride in the mixed gas of helium and oxygen are investigated, and the influences of the oxide scale formed on the surface of zirconium hydride on hydrogen desorption behaviors are also discussed.

2 Experimental

Zirconium hydride samples with hydrogen content of 1.95 H/Zr were directly fabricated from zirconium metal in a modified UHV Sieverts apparatus. The samples were chemical polished for 40 s in the solution of 5%HF-15%HNO₃-80%H₂O (volume fraction) to remove the nature oxides on the surface of zirconium hydride.

The information about dehydrogenation process was obtained by using the technique called gas phase analysis (GPA), where absorption or desorption quantity of various gases are monitored over time by analyzing changes in gas phase with a quadruple mass spectrometer (QMS). Fig.1 shows the experimental apparatus used in the GPA studies. The equipment consists of essentially

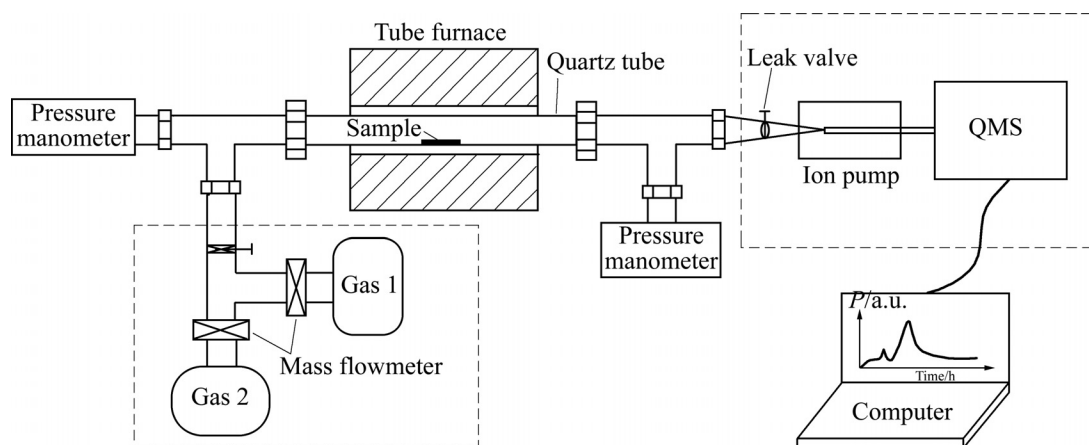


Fig.1 Equipment used in gas phase analysis (GPA) experiment

three parts, a QMS placed in ultrahigh vacuum(UHV), a reaction chamber (consisting of a quartz tube and a tube furnace) and a gas handling system. The equipment allows the inlet of mixed gas from the gas handling system into the reaction chamber. The partial pressures of the gas constituents in the reaction chamber can be analyzed over time with the QMS via a leak valve.

The hydrogen desorption spectra of zirconium hydride at the temperature range from 100 °C to 900 °C in the mixed gas of helium and 5%(volume fraction) oxygen at total pressure of 100 kPa was obtained by the technique of GPA. The heating rate was 5 °C/min in the experiment.

3. Results and discussion

3.1 Desorption behaviors of zirconium hydride

The desorption spectra of zirconium hydride in the mixed gas of helium and 5%(volume fraction) oxygen (abbreviated as He-5%O₂) are shown in Fig.2. Desorption starts slightly above 525 °C and reaches a maximum at 660 °C, but it declines above 660 °C and ends eventually at 800 °C. No hydrogen desorption is observed at the temperature range from 800 °C to 900 °C, but hydrogen evolution restarts at approximately 670 °C during cooling process.

In order to prove the drop of hydrogen desorption that is not due to the consumption out of hydrogen in the sample, the hydrogen desorption spectrum of zirconium hydride in helium was also investigated (Fig.3). Desorption in He produces a broad desorption range, starting slightly above 500 °C and reaching a maximum at the maximum temperature in the experiment (900 °C). Hydrogen evolution still continues during the cooling process and stops at 500 °C, the same temperature of hydrogen starting desorption.

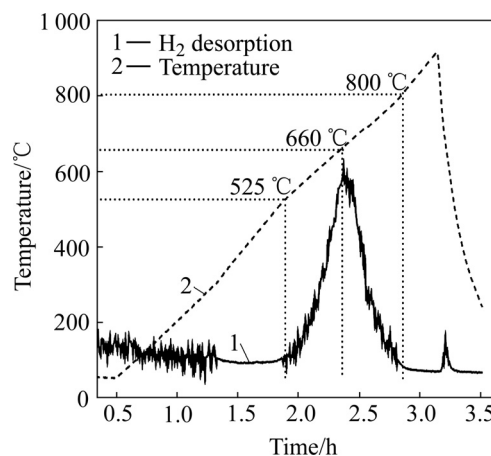


Fig.2 GPA measurements on zirconium hydride in He-5%O₂ at 100 kPa (Heating rate: 5 °C/min)

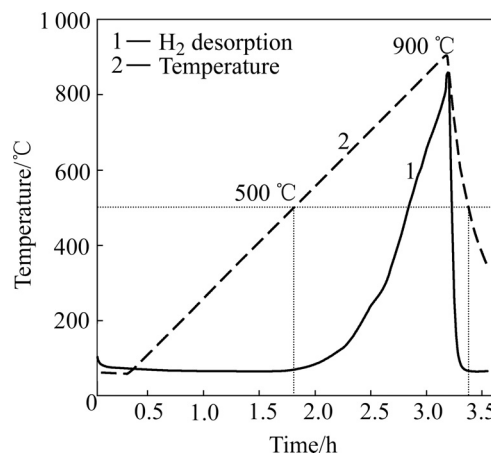


Fig.3 Hydrogen desorption spectrum of zirconium hydride in He at 100 kPa (Heating rate: 5 °C/min)

It can be concluded that the hydrogen desorption is retarded in the presence of oxygen. The different desorption behaviors in He and He-5%O₂ can be explained by the oxidizing influence of oxygen on the zirconium hydride. As far as the restart of hydrogen

desorption in He-5%O₂ during cooling process is concerned, the possible reason is that high cooling velocity could create cracks in the oxide layer which would facilitate gas desorption, but there is no direct proof of this phenomena.

3.2 Thermodynamic calculation of oxidizing reaction

The thermodynamic parameters of the reaction of ZrH₂ with O₂ at different temperatures (as listed in Table 1) were calculated to judge the inclination of oxidizing reaction. The reaction Eqn.(1) of ZrH₂ and O₂ is as follows:



From Eqn.(1) we can see that the resultants are composed of ZrO₂ and H₂O. The oxidizing reaction has a large negative Gibbs energy ($\Delta_r G$) at different temperatures, which suggests the oxidation is thermodynamically possible and occurs more easily with increasing temperature.

Table 1 Thermodynamic parameters of reaction of ZrH₂ with O₂ at different temperatures

$t/^\circ\text{C}$	$\Delta_r H/\text{kJ}$	$\Delta_r S/(\text{J}\cdot\text{K}^{-1})$	$\Delta_r G/\text{J}$
25	-6.01×10^3	-9.83×10^2	-5.72×10^6
200	-5.27×10^3	9.83×10^2	-5.74×10^6
400	-4.56×10^3	2.23×10^3	-6.06×10^6
600	-3.83×10^3	3.18×10^3	-6.61×10^6

In order to obtain a qualitative measure for the oxidation sensitivity of the hydride, an oxygen consumption of zirconium hydride during heating process in He-5%O₂ are given in Fig.4. Hydrogen desorption starts at 525 °C but no significant change of oxygen absorption is observed below 718 °C. It can be concluded that hydrogen released from zirconium hydride in the mixed gas of helium and oxygen has no influence on oxygen consumption. An obviously reduction of oxidation partial pressure presents above 718 °C which suggests a beginning of oxidizing effect. The Gibbs energy of oxidizing reaction at 600 °C is $-6.61 \times 10^6 \text{ J}$ shown as Table 1 and more negative Gibbs energy presents at 718°C, which suggests the oxidation satisfies thermo- dynamic condition but not satisfies kinetic condition.

The H₂O evaporation of the sample during heating process in He-5%O₂ is shown in Fig.5. It can be see that H₂O evaporation is detected only in the temperature range of hydrogen desorption. This indicates that the reaction of ZrH₂ and O₂ does not follow Eqn.(1) but divides into two steps:

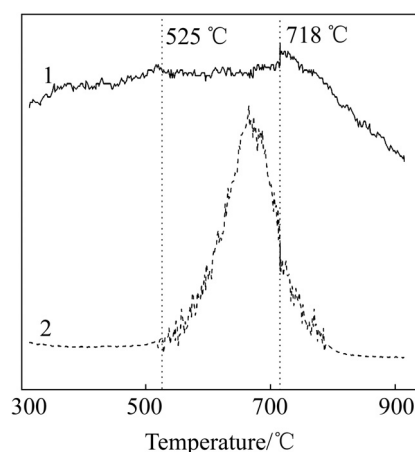


Fig.4 Oxygen consumption of zirconium hydride during heating process in He-5%O₂: 1 O₂ absorption; 2 H₂ desorption

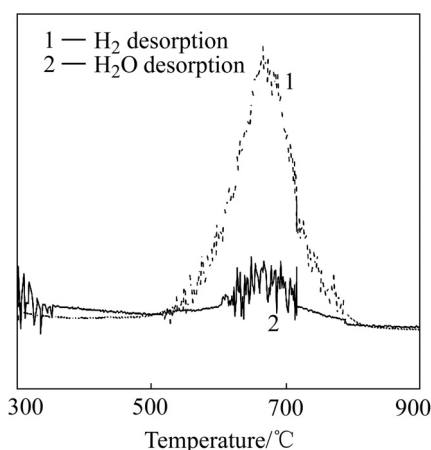


Fig.5 H₂O evaporation of sample during heating process in He-5%O₂

The hydrogen desorption from zirconium hydride synthesizes with oxygen to H₂O as follows:



3.3 Cross-section morphologies of oxide scale

A small amount of oxygen has a great influences on hydrogen desorption behaviors, this can be explained by the forming of oxide scale when zirconium hydride decomposes in an oxygen containing atmosphere. An oxide scale with approximately 20 μm in thickness formed on the surface of zirconium hydride after hydrogen desorption in the mixed gas of helium and oxygen is shown in Fig.6. A loose layer with many holes and cracks presented on the top of the oxide scale, while a dense layer which is compact and holes/cracks free was observed between the loose layer and the bulk metals.

Oxide scales on zirconium hydride modify their hydrogen desorption behaviors because they form an efficient diffusion barrier. The dense layer serves as a protective barrier against hydrogen releasing. Hydrogen

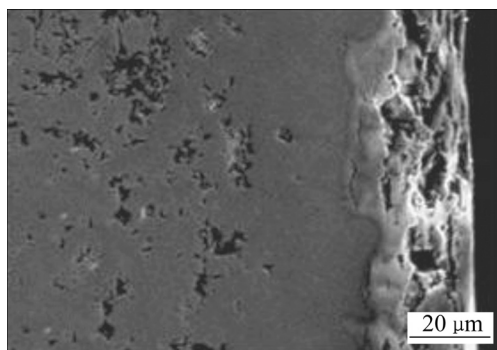


Fig.6 Oxide scale formed on surface of zirconium hydride after hydrogen desorption in He-5%O₂

not only has to diffuse through the bulk zirconium matrix from the inner region towards the surface but also has to overcome the oxide barrier which is an additional kinetic hindrance[9–10].

4 Conclusions

1) Hydrogen desorption is retarded effectively when zirconium hydride is exposed to an oxygen containing atmosphere.

2) The Hydrogen desorption from zirconium hydride in mixture gases of helium and oxygen starts slightly above 525 °C and reaches a maximum at 660 °C and ends eventually at 800 °C. No hydrogen desorption is found at the temperature range of 800–900 °C.

3) Desorption in He has a broad desorption range, starting slightly above 500 °C and reaching maximum at the maximum temperature in the experiment (900 °C).

4) An oxide scale with approximately 20 μm in thickness formed on the surface of zirconium hydride acts as a very effective diffusion barrier.

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