Research on Hydrogen Storage and Delivery Bed at KAERI

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1. Introduction

Nuclear fusion energy research becomes more and more important nowadays. In tokamak-type nuclear fusion reactors, the hydrogen isotope storage and delivery system (SDS) is a part of the nuclear fusion fuel cycle [6]. The SDS metal hydride bed safely stores hydrogen isotopes. We have performed the research on the hydrogen storing materials. Zirconium cobalt (ZrCo) and depleted uranium (DU) were used as storing materials [2]. The ZrCo and DU characteristics are introduced. The performance of hydriding and dehydriding of DU bed is presented. Furthermore, tritium accounting was studied. Measuring of the tritium amount left in the SDS bed is important in the operation of the nuclear fusion fuel cycle. The tritium accounting was performed by using an in-bed calorimetry method. The calibration curve was obtained consists of tritium amount versus the SDS bed temperature. In this paper, the hydriding and dehydriding performance of DU is presented and the tritium accountability calibration curve is shown. We also suggest further experimental plans related to the filter effects on hydrogen delivery rates in conclusion.

2. Hydrigiding and Dehydriding Performances of Hydrogen Storing Materials

In this section, ZrCo and DU were used to store hydrogen in the system. Characteristics of ZrCo and DU were described as well as the hydriding and dehydriding performance of these storing materials in SDS bed.

2.1 Reactions of Zirconium Cobalt and Depleted Uranium with Hydrogen

The reactions between ZrCo and hydrogen, including hydriding, dehydriding, disproportionation, and regeneration are shown in equation 1-4 [1]. These equations show only hydrogen, however, the reaction between deuterium and tritium also can be shown as stoichiometric ratio reaction with ZrCo.

$$ZrCo(s) + H_2(g) \rightarrow ZrCoH_2 \quad (1)$$

$$ZrCoH_2 \rightarrow ZrCo(s) + H_2(g) \quad (2)$$

$$ZrCoH_2 \rightarrow 0.5ZrH_2 + 0.5ZrCo_2(s) + 0.5H_2(g) \quad (3)$$

$$ZrH_x + ZrCo_2(s) \rightarrow ZrCo(s) + H_2(g) \quad (4)$$

The equation 1 shows hydriding stage of ZrCo at room temperature. The equation 2 shows the dehydriding stage of ZrCo at temperature 250℃ - 350℃ under vacuum pumping. The equation 3 shows the disproportionation stage of ZrCo at over temperature 380℃ under equilibrium pressure. The equation 4 shows the regeneration stage of ZrCo at over 500℃ under vacuum pumping. Since ZrCo is intermetallic compound, it dispersed into Zr and Co by repeating the hydriding and dehydriding cycle in high temperature. According to Shim's paper, the ZrCo almost dispersed into $ZrCo_2$ and ZrH_x over 380℃. Figure 1 and 2 show the x-ray diffraction results of ZrCo disproportionation at 380℃ and 400℃ respectively [5]. This data represent storing material ZrCo decrease by running the cycles.

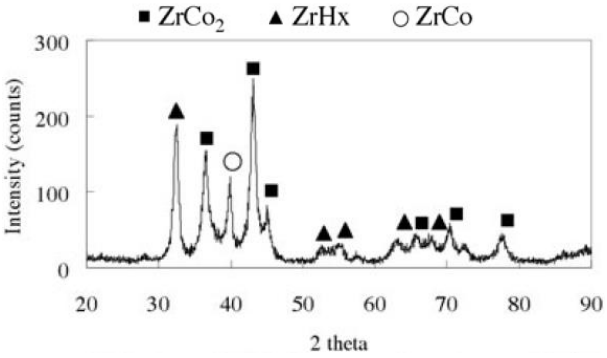

Fig. 1. X-ray diffraction of ZrCo disproportionation at 380℃ [5]

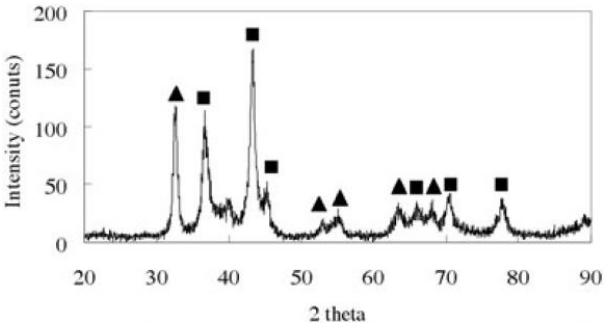

Fig. 2. X-ray diffraction of ZrCo disproportionation at 400℃ [5]

Even though the ZrCo and hydrogen reaction have regeneration process at high temperature over 500℃, it decreases in efficiency of storing and delivering hydrogen. Also, it is safer to keep the operating temperature lower.

The reaction for uranium hydride formation is given by the equation:

$$U(s) + H_2(g) \rightarrow UH_x \quad (5)$$

$$UH_x \rightarrow U(s) + H_2(g) \quad (6)$$

The equation 5 shows the hydriding stage of DU at room temperature and equation 6 shows the dehydriding stage of DU at high temperature [4]. The hydrogen atoms go into lattice structure of DU on the interstitial sites at room temperature.

Table. I: Gibbs free energy in the temperature range 400℃ to 406℃ [4].

Temperature(℃)	ΔG(kcal/mol)
400	-0.118
401	-0.070
402	-.0.022
403	0.026
404	0.074
405	0.121
406	0.169

Table 1 shows the Gibb's free energy in the temperature range 400℃ to 406℃ [4]. It describes uranium is spontaneous absorbing hydrogen until 402℃ and at higher temperature the uranium desorb hydrogen from uranium interstitial sites. This result can be used as fiducial point to determine hydriding and dehydriding.

2.2 Hydriding and Dehydriding Performance of DU Material

Figure 3 shows the ratio of hydrogen absorption in the storage material UH_x over time. It shows hydriding time has been reduced by overrun the hydriding. It can be assumed hydriding and dehydriding process makes compound or metal brittle which become micron-size particle. It increases the surface area follows with increase in reaction time. Therefore, powderization of the material affects to the performance of hydriding. The DU chunk has processed powderization by repeating hydriding and dehydriding 3 to 5 times.

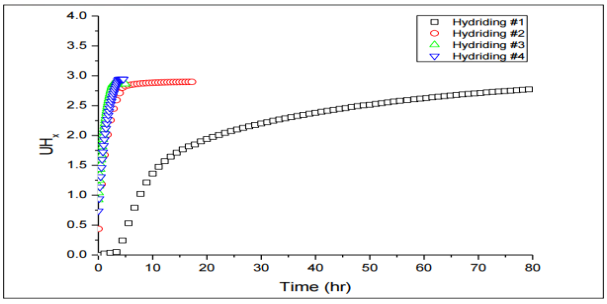

Fig. 3. Ratio of hydrogen absorption in the UH_x

Figure 4 shows the changes of pressure and temperature during the hydriding. The pressure indicates the hydrogen pressure in the SDS bed. The temperature has increased until around 90℃ in hydriding process which can be explained by Gibbs free energy. The pressure of the SDS bed has been rapidly increased when it reaches to 95% of maximum hydriding. Figure 5 shows the changes of pressure and temperature during the dehydriding. The result shows some pressure overshooting at the blue circled moment. The dehydriding temperature goes up to 450℃ and the pressure of SDS bed took about 6 hours to converged with the pressure of measuring tank.

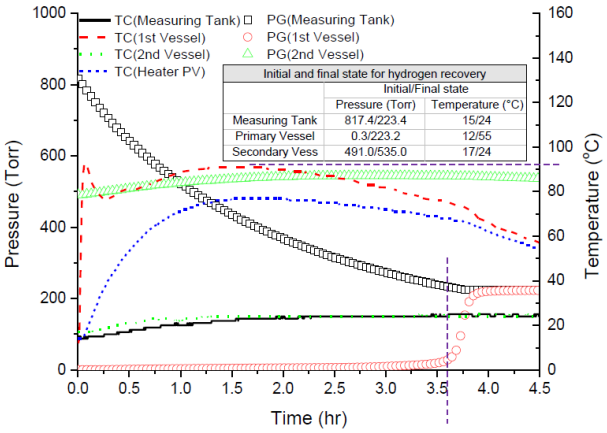

Fig. 4. Changes of pressure and temperature during the hydriding

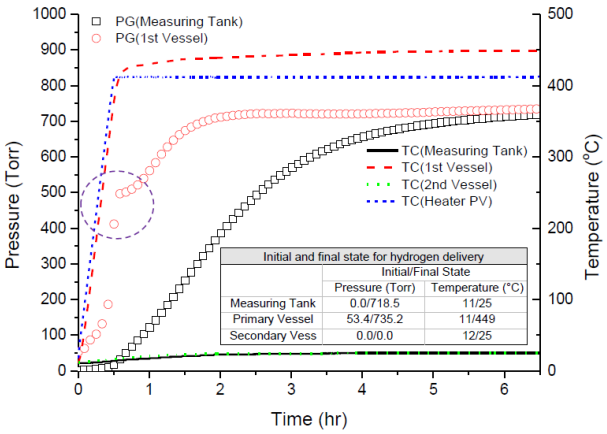

Fig. 5. Changes of pressure and temperature during the dehydriding

3. Tritium Accounting in DU Bed using In-Bed Calorimetry

Tritium and deuterium which are hydrogen isotopes are main fuel of nuclear fusion reaction. In operation of nuclear fusion reactor, these hydrogen isotopes are supplied from SDS bed. It is important to measure the amount of left fuel and in-bed calorimetry is one methodology to measure the amount of hydrogen isotopes. The amount of tritium in the bed can be

indirectly obtained by measuring the tritium decay heat. Tritium emits 0.324 W/g of decay heat and figure 6 shows the temperature of the uranium hydride bed according to the decay heat tritium amount under steady-state conditions [3]. This result shows that the calorimetry methodology can be applied for tritium inventory measurement.

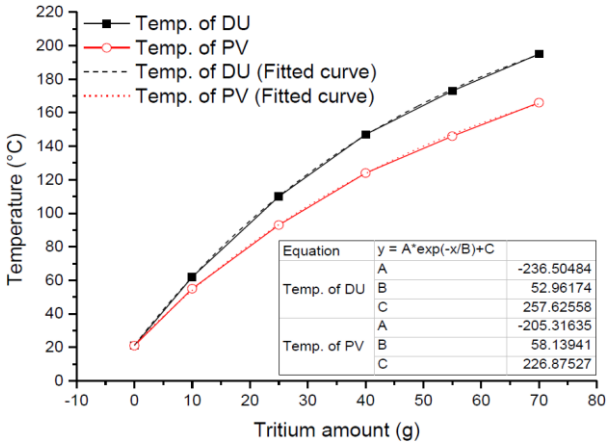

Fig. 6. Temperature of the uranium hydride bed according to the decay heat tritium amount under steady-state conditions [3]

4. Conclusions

The characteristics of DU and ZrCo are introduced and hydriding and dehydriding performance of DU is presented. Due to the disproportion of ZrCo, it is better to use DU as storing material. The advantage of using DU as a hydride material is it has a low equilibrium pressure at room temperature, thereby minimizing hydrogen isotopes loss when the manifolds of the storage system are purged. Despite the advantages, repeating hydriding and dehydriding process, DU tends to break up into fine sub-micron sized particles which can contaminate system for the fragments. Since the filter is used to prevent small particles entering into the system. The filtering system in the SDS will be performed for further experiment.

ACKNOWLEDGMENTS

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