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Investigation of a Possible ZrCo Disproportionation under the SDS Bed Operating Conditions

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1. Introduction

In the ITER (international thermal experimental reactor), the KAERI has full responsibility for the R&D of SDS beds. ZrCo was selected as the ITER reference material for the metal hydride storage beds. The disproportionation reaction of ZrCoHx has been reported to occur at a high temperature (>=400^{o}C) and a high hydrogen pressure (more than equilibrium pressure) with the (1)-(2) equations [1-3].

$2ZrCoHx \rightarrow ZrH_2 + ZrCo_2$ (1)

$2ZrCoHx \rightarrow ZrH_2 + ZrCo_2 + 2(x-1)H_2$ (x>1) (2)

$2ZrCoHx + 2(1-x)H_2 \rightarrow ZrH_2 + ZrCo_2$ (x<1) (3)

ZrCo disproportionation rate at a temperature lower than 400^{o}C was extremely slow [3]. Also, a disproportionation was not observed in pressure lower than the equilibrium pressure because a dehydriding reaction of the (4) equation is much faster than the disproportionation reaction [3].

$2ZrCoHx \rightarrow ZrCo + x/2H_2$ (4)

Disproportionated ZrCo was completely regenerated to ZrCo at 500^{o}C under a vacuum pumping and the hydriding capacity was the same as the ZrCo before the disproportionation [3].

Disproportionation characteristics of ZrCo were examined at a higher temperature (400-450^{o}C) [1-3]. For the delivery of the ZrCo SDS bed, the maximum temperature is 350^{o}C (250-350^{o}C) under a vacuum pumping without a disproportionation. In order to determine the optimum SDS operating temperatures, a disproportionation of ZrCo should be carefully examined. In the present study, a ZrCo disproportionation was examined at temperatures (< 400oC) to be applied to the SDS/LTS beds.

2. Experimental

The experimental apparatus used for the present study has been reported by S. Paek et al. [4]. The temperature of the reactor was measured by a K-type thermocouple attached onto the outer surface of the reactor. Hydrogen gas pressures were measured by MKS Baratoron. Signals of the thermocouple and pressure/vacuum gauges were continuously monitored using the Labview software.

ZrCo chunks (SAES Getters Milano, 60.8wt% Zr, 39.2wt% Co, 1-2mm thickness and 10-15mm width) were placed in a vertical cylinder(ID=13mm, t=2mm, h=330mm). High purity hydrogen (99.999%) gas was used after passing it through moisture and oxygen traps. ZrCo was reacted with the hydrogen ingressed through a 2μm porous stainless steel filter on the top of the reactor. This reactor was heated by an electric furnace and a PID programmable controller controlled the temperature.

For the evaluation of a disproportionation at 375^{o}C, 0.9g ZrCo chunks was activated by three repetition of hydriding and dehydriding（Table 1）. ZrCo was hydrided to $ZrCoH_{2.5}$（Table 2）. In the closed volume (164.4cm^3), the reactor was heated to 375^{o}C and the pressure change was examined.

Table 1. Activation of 0.9g ZrCo chunks

pretreatment	At 400^{o}C, under TMP pumping for 2 hours
Hydriding 1	$[H_2]$initial = 785torr(30H/ZrCo), at 100^{o}C
Hydriding 2	$[H_2]$initial = 785torr(30H/ZrCo), At room temperature
Hydriding 3	Same to hydriding 2
Three dehydridings	At 350^{o}C, under rotary pumping, For 1.5-2 hours

Table 2. Hydriding and disproportionation

Hydriding	$[H_2]$initial = 1036torr(2.5H/ZrCo) At room temperature
disproportionation	375^{o}C/30min, 375^{o}C for 5 days in the closed volume(164.4cm^3)

3. Disproportionation of ZrCo

Disproportionation kinetics of ZrCo can be explained by the Avrami-Erofeev equation [3].

$$б = 1- \exp\{-(t/\tau)^n\} \quad (5)$$

б represents the ratio of the disproportionation estimated for the pressure change by reaction (2) and (3). τ means the time of a 63.2% disproportionation and t is the time.

Under 1000torr of hydrogen of 400^{o}C, ZrCo disproportionation started at about 25 hours and a 63.3% disproportionation occurred after 83.3 hours [3]. The disproportionations at 200-400^{o}C can be interpolated at 1000torr hydrogen under the conditions shown in Figure 1-2 and Table 3. In the case of the ITER SDS operation at delivery for 8hr/day, 10% ZrCo disproportionation was expected after 30.9 days at 350°C and after 237.8 days at 300°C under 1000torr hydrogen. In the ITER SDS operation, ZrCo will be preheated to 250-300°C before shots and supplied to the SDS reservoir at 300-350°C under a vacuum pumping. So, the expected disproportionationed ZrCo should be regenerated at 500°C under a vacuum pumping periodically two times per year.

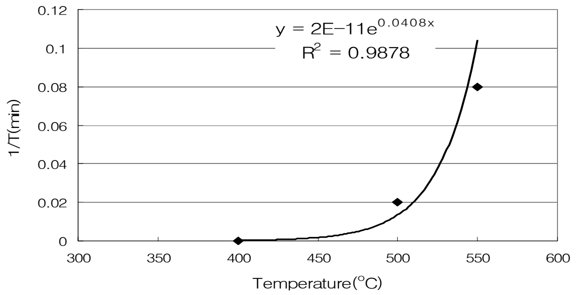

Figure 1. Disproportionation under 1000 torr H_2 started from ZrCo

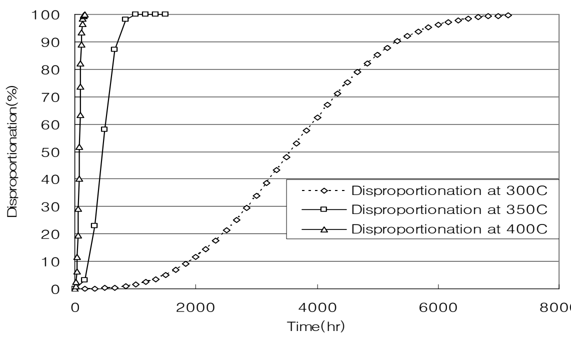

Figure 2. Expected disproportionation at 300, 350, 400°C under 1000torr H_2 started from ZrCo

Table 3. Interpolated and Expected disproportionation under 1000torr H_2 started from ZrCo

Temperature	10% dis*	10% dis**	63.2% dis***
250°C	1828.7 days	609.6 days	1290.6 days
300°C	237.8 days	76.3 days	167.8 days
350°C	31.7 days	10.3 days	21.8 days
375°C	11.15 days	3.72 days	7.9 days
400°C	4.92 days	1.64 days	3.5 days

10% dis* : 10% disproportionation for 8hours/day in ITER operation
10% dis**: 10% disproportionation
63.2% dis***: 63.2% disproportionation

Experimental disproportionation at 375°C was examined in Figure 3(Table 2) and compared to the interpolated and expected disproportionation in Figure 4. Disproportionation started after 2 days. 10% and 63% disproportionations occurred after 2.64days and 4.82days respectively. From this experiment, $ZrCoH_{1.35}$ was disproportionated to $ZrCoH_{1.11}$ by the (2) equation. In a closed volume, the pressure increased from 395.5torr to 466.8torr at room temperature.

The pressure of ZrCoHx increased from 853.9torr to 1010.6 torr. At 375°C, the experimental disproportionation rate was faster than the interpolated disproportionation under 1000torr H_2 started from ZrCo.

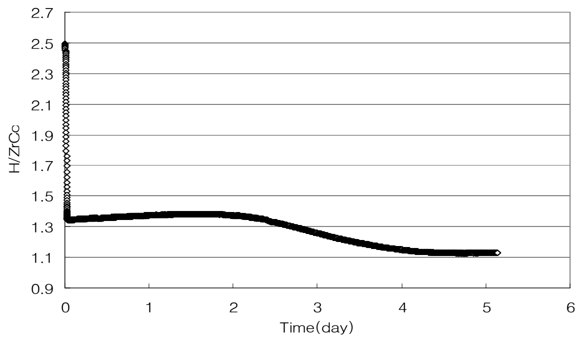

Figure 3. Disproportionation at 375°C

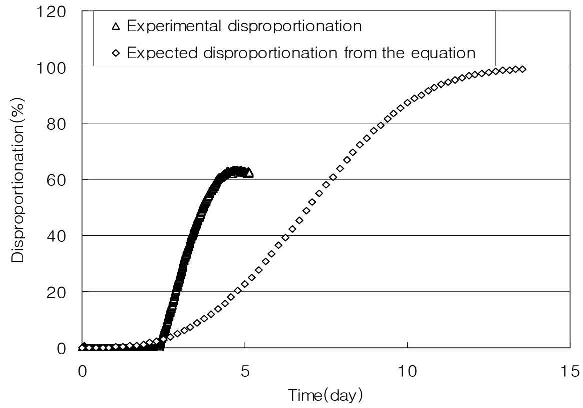

Figure 4. Comparison of experimental and expected disproportionations at 375°C

4. Conclusion

From this result, ZrCoQx(Q=H, D, T) should be delivered under a pumping at <350°C. In a closed volume, the temperature of ZrCoQx should be below 300°C. The present study is on going to investigate the disproportionation rate at lower temperatures (250-350°C) to determine the optimal operating conditions of the SDS and LTS to avoid a ZrCo disproportionation for successful SDS and LTS operation.

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